

Coating of Anodes to Reduce Air Oxidation

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Abstract

The three major factors that contribute to high net carbon consumption are air burn, reaction with carbon dioxide and carbon dusting. Baked anodes are subjected to air oxidation mainly because of improper covering and redressing activities, porosity and thermal conductivity of the baked anodes and presence of chemical catalysts. Air burn leads to higher top oxidation and reduced butt weight, which in turn increases carbon dioxide emissions. However, using a coating material on the top and the four sides of the anodes can help prevent severe air burn by forming a barrier against the penetration of oxygen inside the pores, thereby reducing the top oxidation by 3-4 mm and increasing the butt weight by 15 kg, and increasing the air reactivity residue. The application of this coating material can reduce the cut-butt percentage significantly, especially for the anodes near breakers, help improve the butt profile, and reduce carbon footprint by a significant amount. Several trials have proved that there is no impact on the pot parameters like noise, voltage, bath temperature, excess AlF_3 and anode top temperature. The coating material does not affect the metal purity nor the covering material composition and chemical composition of the anode butts. Unlike other conventional methods to reduce air burn, the application of this coating material offers several advantages from economic as well as safety point of view.

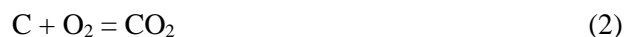
Keywords: Net carbon consumption, Air burn, Anode top oxidation, Butt weight, Carbon footprint.

1. Introduction

In an electrolytic cell, the theoretical carbon consumption for producing 1 t of aluminium is 334 Kg, according to the reaction:



However, the net carbon consumption (NCC) is much higher, mainly due to air burn, carboxy reaction and dusting [1], and varies typically, between 400-450 kg C/t Al. The chemical reaction of air burn is given by:



The presence of chemical catalysts like iron, vanadium, titanium, nickel, calcium, sodium, lead, copper, zinc, etc., further aggravates the air burn. The most widely followed practice in aluminium smelters to prevent air burn is by covering the surface and sides of the anodes with a layer of crushed bath and alumina (28-35 % of alumina). However, sometimes due to improper covering of the new anodes or due to improper redressing of anode cover, the anodes, especially near the breaker region are subjected to a high amount of air burn, which in turn reduces the net carbon consumption.

There will be air burn of the baked anodes at temperatures above 450 °C if there is enough air access to the anodes and as the temperature of the anodes increases, the intrinsic air burn rate

increases rapidly, following a typical Arrhenius exponential plot. The air burn reaction can be classified into three major zones: (a) diffusion-controlled (b) mixed zone and (c) reaction-controlled zone. At around 600 °C, the reaction rate becomes controlled by the rate of supply of oxygen gas and it typically depends on the integrity of the anode cover; anode properties have little role, in such a case. However, if it is possible to cover the pores of the anodes properly, with the help of a coating material, the supply of oxygen gas to the pores will be cut off, thereby reducing the risk of air burn.

To date, a large number of techniques have been employed by smelters worldwide to reduce air burn, like use of aluminium spray on the surface of the anodes [2], addition of boric acid to the anode paste [3, 4], but each technique, has its own inherent limitations, either due to safety hazards or due to impact on metal purity.

In this paper, we will show the results of alumina-based coating [5]. In our case, a 1 to 1.5 mm thick alumina-based coating, when applied properly, has been found to sufficiently reduce the cut butt percentage, reduce the top surface oxidation and increase the butt weight, thereby reducing the carbon footprint of the aluminium smelting process. The drying and curing time of the coating, although dependent on the relative humidity (RH), has been found to be fully cured in no more than two hours with air drying. The coating has been found to last more than a week and has been effective in reducing the high air burn in the crust breaker regions. Also, since there is a delay of about 4-8 hours, after anode change before covering the new anodes, this coating has been found to be effective in stopping the air burn between the completion of the anode change and covering of the new anodes.

2. Experimental Procedure

A systematic procedure was adopted for testing the integrity of the in-house developed coating solution for baked anodes. At first, a laboratory-scale trial (Stage-1) was conducted to assess the performance of the coating material. Two samples of drilled anodes were coated with coating recipe of different compositions by weight. Along with a normal non-coated drilled baked anode sample, the three samples were subjected to an air reactivity residue (ARR) test in the laboratory for 10 hours at 550 °C as shown, in Figure 1.

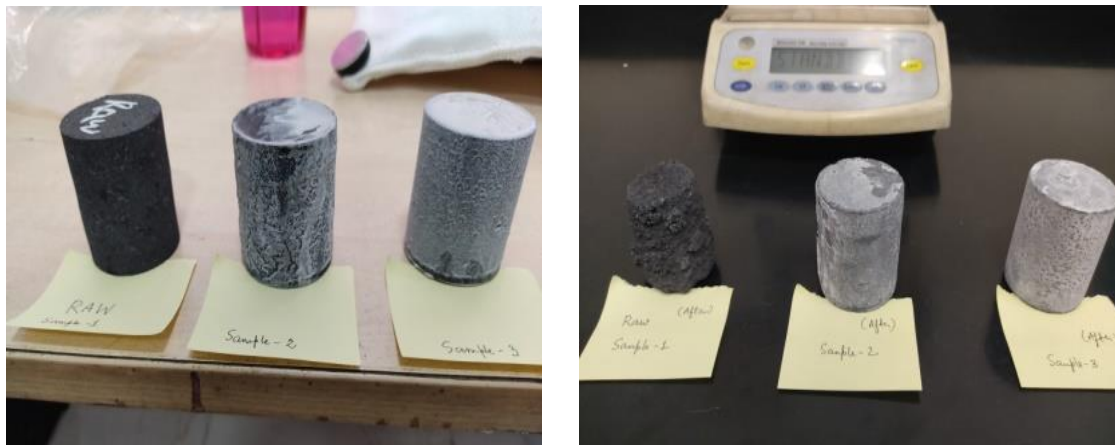


Figure 1. Air reactivity test of coated anode samples. Left: before, Right: after.

Following the lab scale trials, the constituents were mixed thoroughly, using an agitator in order to ensure homogeneity and the coating trial was manually applied on the surface of the previously weighed baked anodes on the top (excluding the cast iron collar) and the long sides and the short sides and the anode samples were used in a total of four pots in two plants for two anode change cycles (Stage-2). Pot parameters, such as anode current density, pot average voltage, noise, bath

temperature, excess AlF_3 , anode cover height, anode top surface temperature, metal purity, anode cover bath composition were recorded, and daily audit of the covering integrity and air burn of the selected pots was conducted. The anodes were marked with different colours on the stems for ease of identification in the rodding shop. The coating was applied in such a fashion that there was no visible carbon on the coated anode surface and sometimes double coating was applied with thickness no more than 1.5 mm to ensure uniform coating. After sufficient drying time, the anodes were sent to the potline for trial.



Figure 2. Coated anode sample. Left: Top View, Right: Side View.



Figure 3. Coated anode sample condition inside pot. Left: After anode change, Right: Tap end.



Figure 4. Coated anode condition (1 week old).

After the completion of the anode change cycles, the butts were tracked in the rodding shop for butt dimension, butt weight and anode top oxidation measurement, and the butt samples were sent to the lab for checking the impurity percentages in the butt samples. After encouraging results were obtained in the lab-scale trial and the small-scale trial, a proper design of experiment was prepared for the trial and a bench-scale trial (Stage-3) was conducted in one full section for two cycles of anode change. In this trial two sections were chosen, one labeled as the trial section and the other as the reference section, both belonging to the same potroom in the potline and having similar cathodes, pot age, last six months similar AlF_3 consumption, and the same fume treatment plant. The coated anodes were used exclusively in the trial section and normal anodes from the same batch, having similar baked anode weights, were used in the reference section. All the above mentioned parameters were tracked in both sections and anode covering audit was done each second day in both the sections.

Around 4 000 coated anodes and a similar population of non-coated anodes were consumed in the trial. More than 50 % of butts of the trial section and the reference section were processed in the rodding shop. Also, during the trial, a study was conducted in one of the pots in the trial section where the coated anode butts were removed from the pot and the butts were weighed and their top oxidation was measured to find a correlation with anode age. Also, with drilled baked anode samples, a drying time study was conducted in a curing oven to ensure optimum drying time and parameters and to ensure that there was no effect on rodding shop cycle time during the scale up.

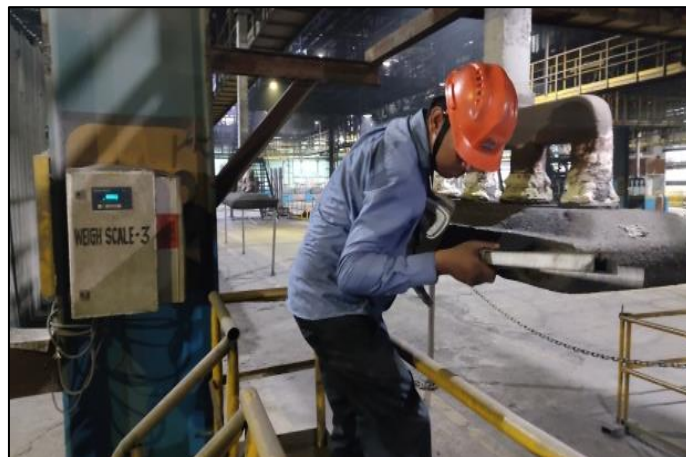


Figure 5. Butt dimension measurement.

3. Results and Discussion

3.1 Lab-Scale Trial (Stage-1)

As can be seen from Table 1, both coated anode samples have high air reactivity residue values compared to the non-coated sample.

Table 1. Lab Scale test results.

Sample ID	ARR (air reactivity residue) (%)	ARD (air reactivity dust) (%)	ARL (air reactivity loss) (%)
Sample-1 (non-coated)	61.35	12.71	25.94
Sample-2 (coated)	96.34	0.52	3.14
Sample-3 (coated)	95.80	1.39	2.80

Also, physical tests of coated anode samples such as porosity and electrical conductivity showed very encouraging results. The percentage of dusting and loss due to reactivity was greatly reduced due to the presence of coating.

3.2 Small Scale Trial (Stage-2)

3.2.1. Anode Cover Bath Analysis Report

The cover bath analysis report shows that there is no effect of the coating material on the impurity percentage as can be seen in Table 2 and Table 3. The coating material has an average life of around seven days inside the pot.

Table 2. Cover bath analysis report (Plant-1).

Sl. No	Sample ID	% Fe ₂ O ₃	% SiO ₂
1	XY38 B10g	0.119	0.182
2	XY37 A8g	0.117	0.203
3	XY37 B9g	0.139	0.218
4	XY37 B1g	0.118	0.185
5	XY37 B6g	0.111	0.173
6	XY38 A3g	0.110	0.158
7	XY38 A9g	0.120	0.164
8	XY38 B6g	0.111	0.163

Table 3. Cover bath analysis report (Plant-2).

Sl. No.	Sample ID	% Fe ₂ O ₃	% SiO ₂
1	ZZ04 A5g	0.137	0.231
2	ZZ06 B2g	0.121	0.243
3	ZZ06 A2g	0.095	0.203
4	ZZ06 B5g	0.108	0.221
5	ZZ04 B5g	0.119	0.284

3.2.2. Anode Butt Chemical Analysis Report

The spent anode chemical analysis report shows that all the impurities are well within acceptable limits and evidently there is no effect of coating on the spent anode chemical composition. The difference in impurity content in the butt composition in plant-1 & plant-2 are mainly different due to slight differences in baked anode impurity percentages, mainly vanadium, titanium and nickel

Table 4. Butt chemical composition.

Sl. No.	Iron	Silicon	Titanium	Vanadium	Nickel	Sodium	Calcium	Zinc
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1(p-1)	586	85	4	263	143	158	136	40
2(p-1)	684	101	4	234	115	74	209	41
3(p-2)	589	95	11	279	176	292	199	45

3.2.3. Pot Parameter Trend

As can be seen from the trends of the parameters such as average voltage, noise, bath temperature, it can be safely concluded that the coating does not affect the pot parameters.

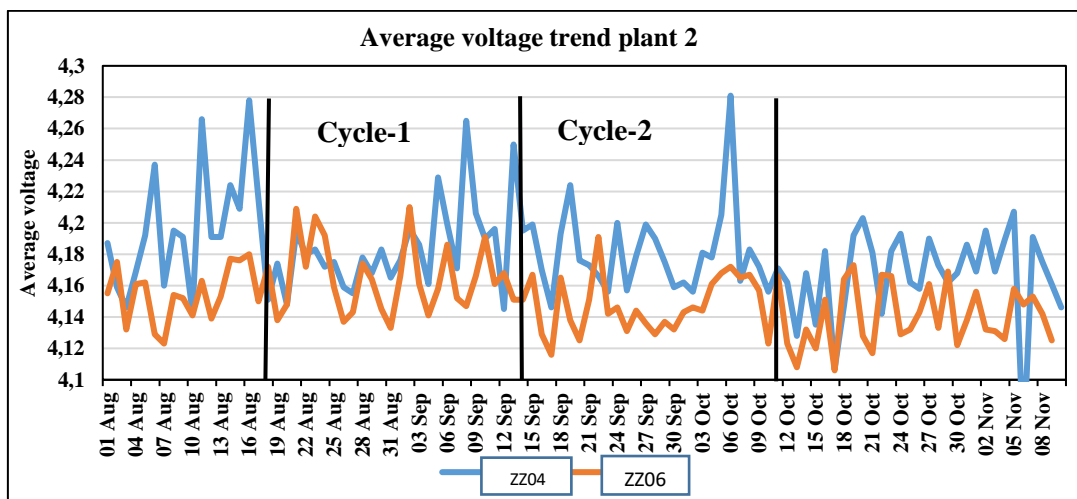


Figure 6. Average voltage trend.

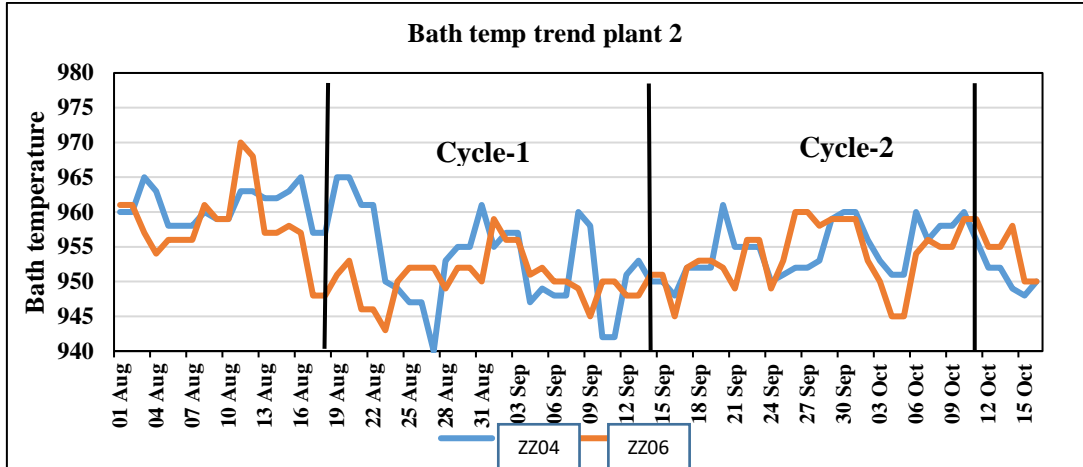


Figure 7. Bath temp trend.

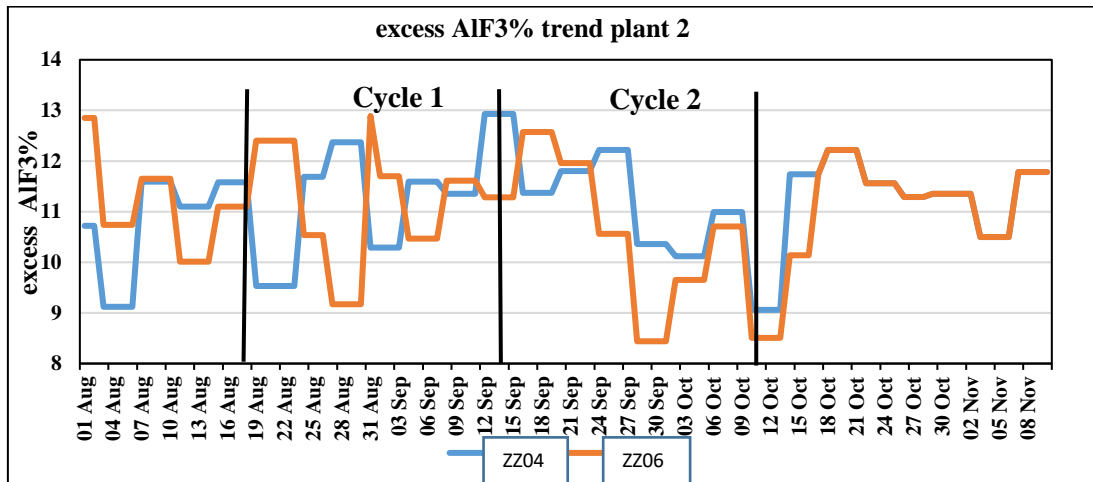


Figure 8. Excess AIF₃ trend.

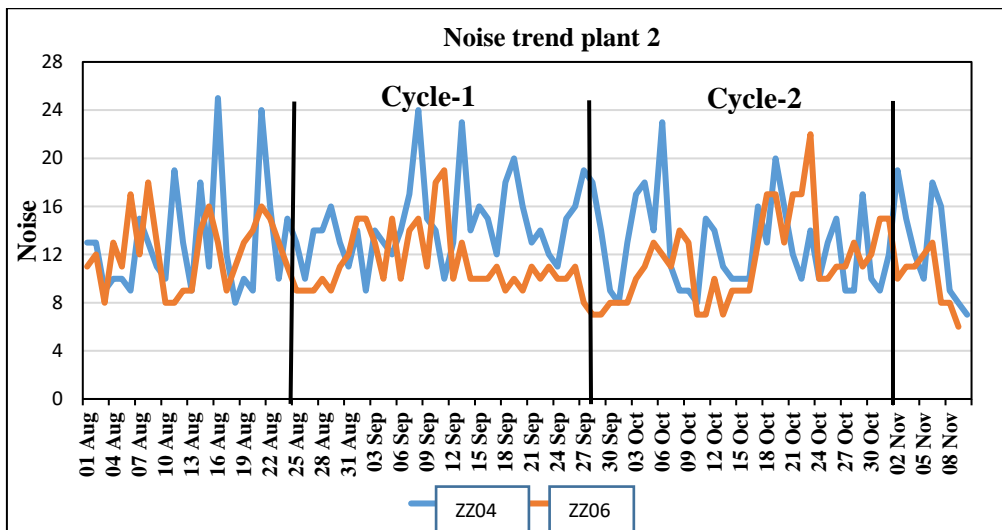


Figure 9. Noise trend.

3.2.4. Anode Butt Profile and Top Oxidation

Figures 10-13 indicate a good butt profile with much less top oxidation and higher butt weights. The anodes near the breaker region also showed less air burn and had better butt profile than their non-coated counterparts. This gain in butt weight and less oxidation have been consistent in both, the small-scale as well as the bench-scale trial.



Figure 10. Coated anode butts. Left: Butt Profile, Right: Top oxidation.

As can be seen from the bar charts of Figures 11 and 12, there is a clear gain of 15 kg in butt weight and 3.1 mm less top oxidation. Also, the graphs below indicate age-wise trend of butt weight of the coated anodes and their top oxidation values, respectively.

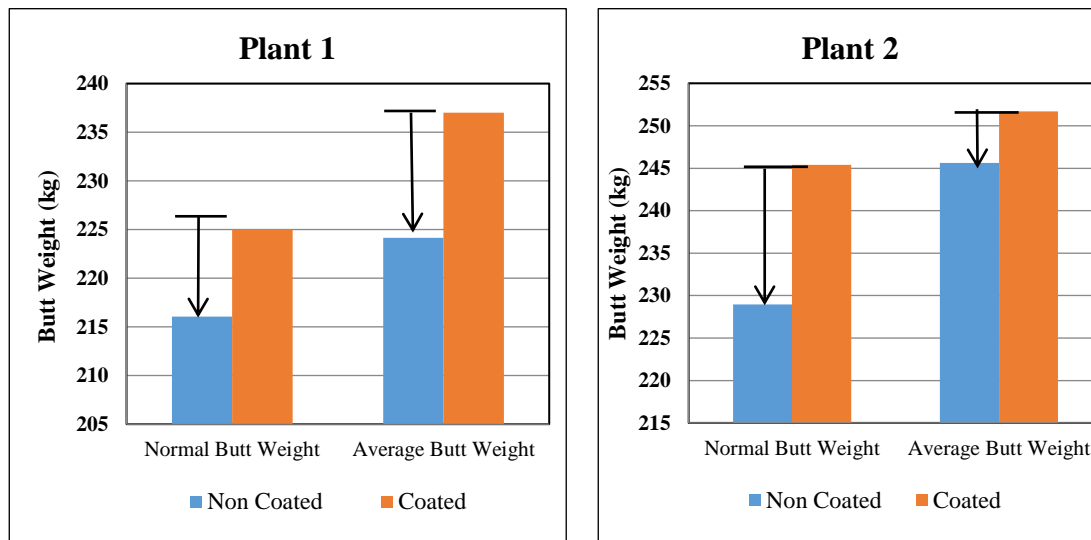


Figure 11. Butt weight gain. Left: Plant-1, Right: Plant-2.

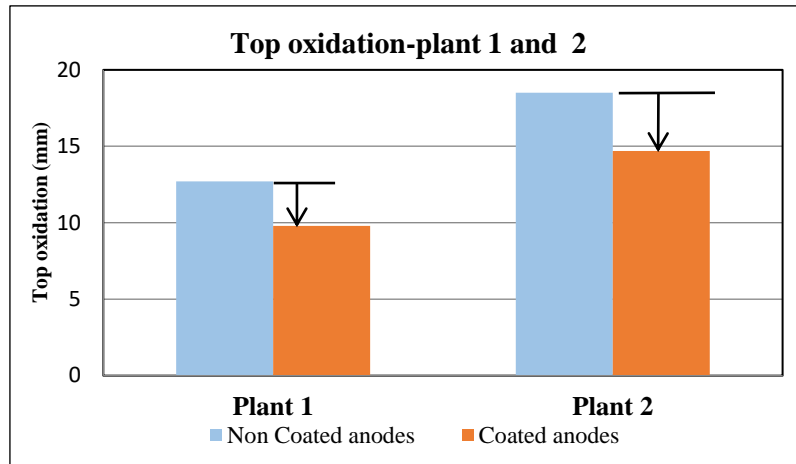


Figure 12. Top oxidation gain.

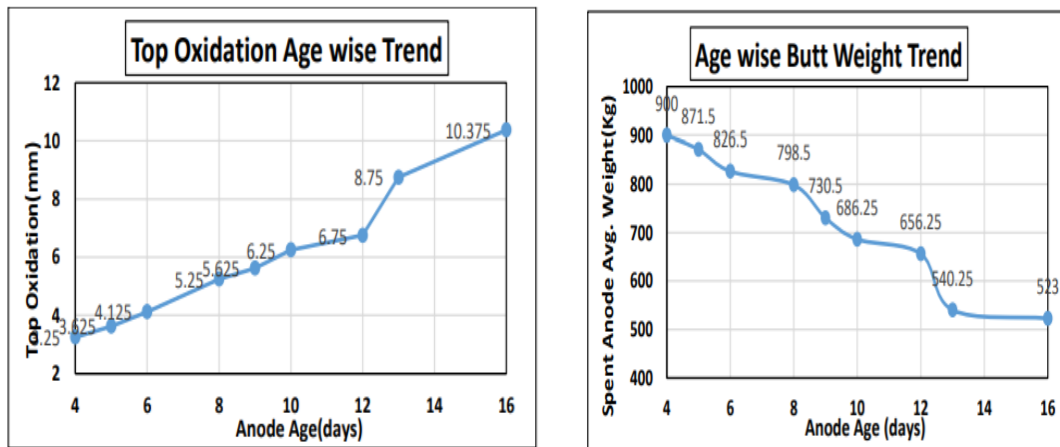


Figure 13. Age-wise butt weight and top oxidation trend.

3.2.5. Drying Time Study

In this study, the coated anode samples were subjected to drying without any air circulation and were heated to three different set temperatures, 50 °C, 75 °C and 100 °C in a hot air oven. The drying time study was repeated three times and, in all cases, the minimum drying time was 5 to 7 minutes at 100 °C, 10 minutes at 75 °C and at 15 minutes at 50 °C. From power consumption point of view, the optimum drying temperature was found to be 75 °C and further reduction in drying time would be possible with hot air circulation. However, for air drying of the coated anodes having large surface area, around two hours is sufficient for complete air drying.

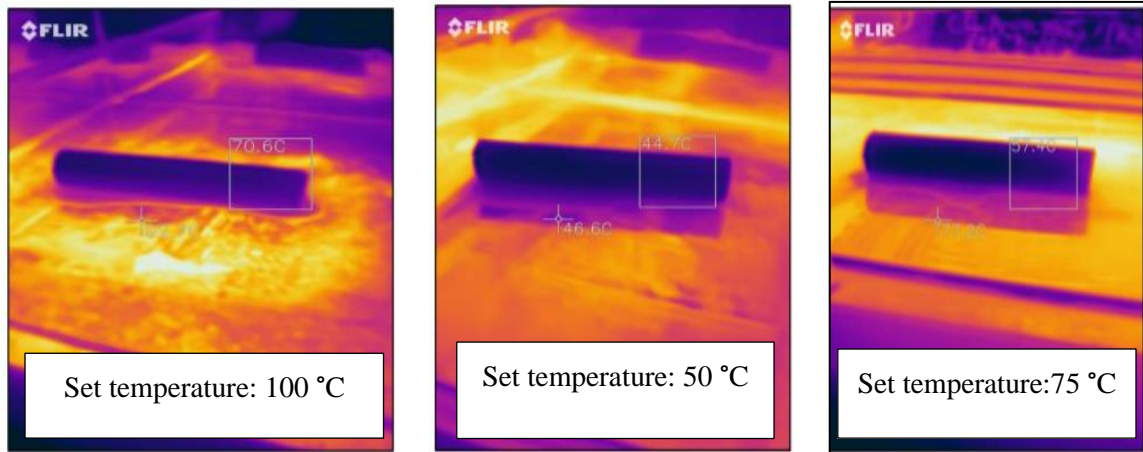


Figure 14. Drying time study at different temperatures.

3.3 Large Scale Trial (Stage-3)

Figures 15-20 show the trend of the tracked pot parameters in the trial section as well as the reference section for two anode change cycles. All the parameters have been found to be well within range, which clearly indicates that the coating material has no negative impact on the pot parameters.

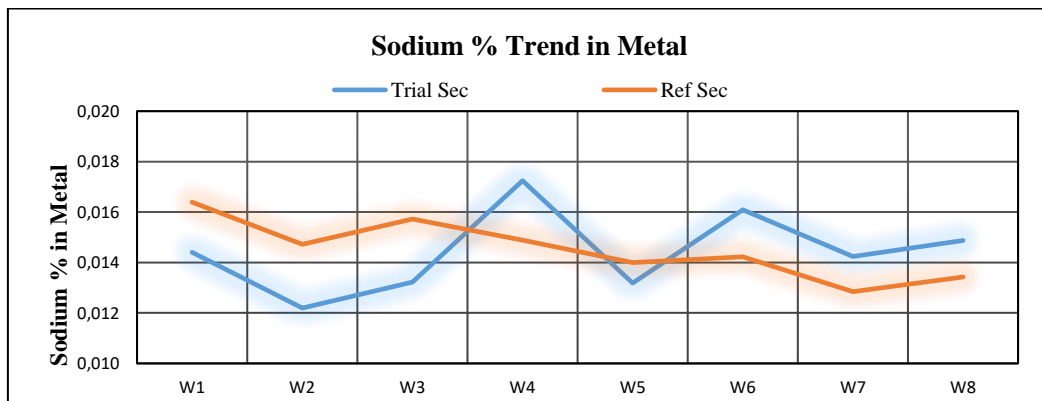


Figure 15. Average sodium% weekly trend (Sec = Section).

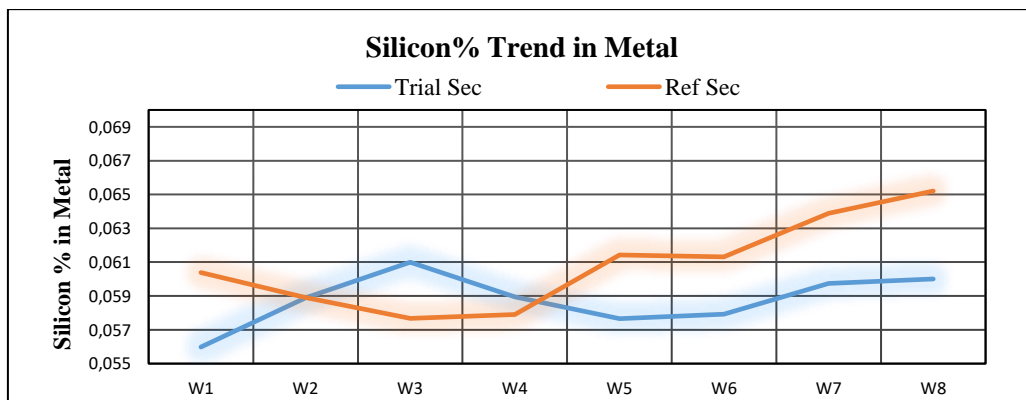


Figure 16. Average Silicon% Weekly Trend (Sec = Section).

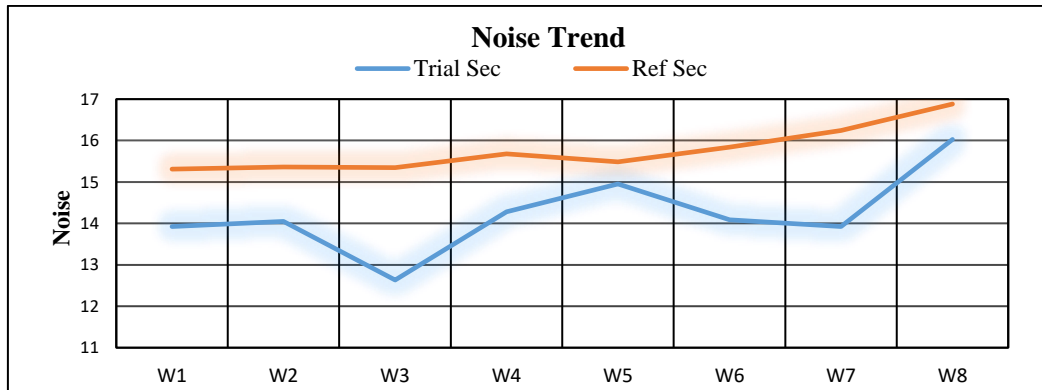


Figure 17. Average noise weekly trend (Section).

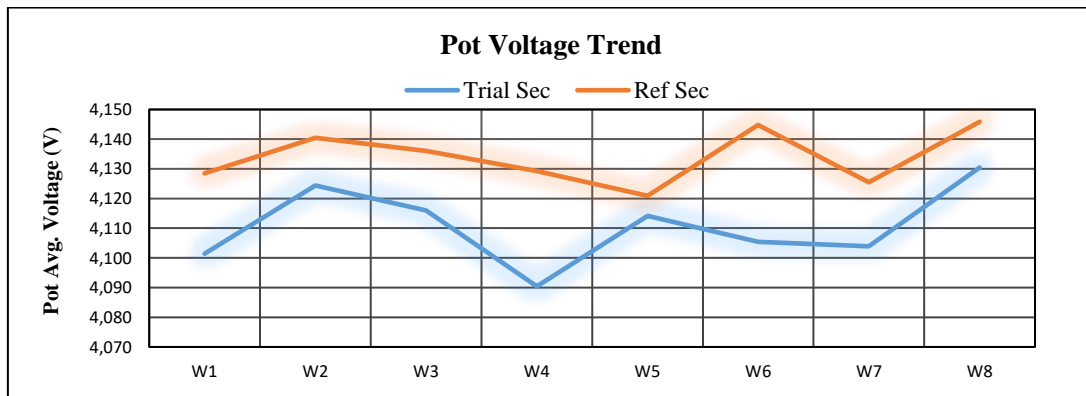


Figure 18. Average pot voltage weekly trend (Sec = Section).

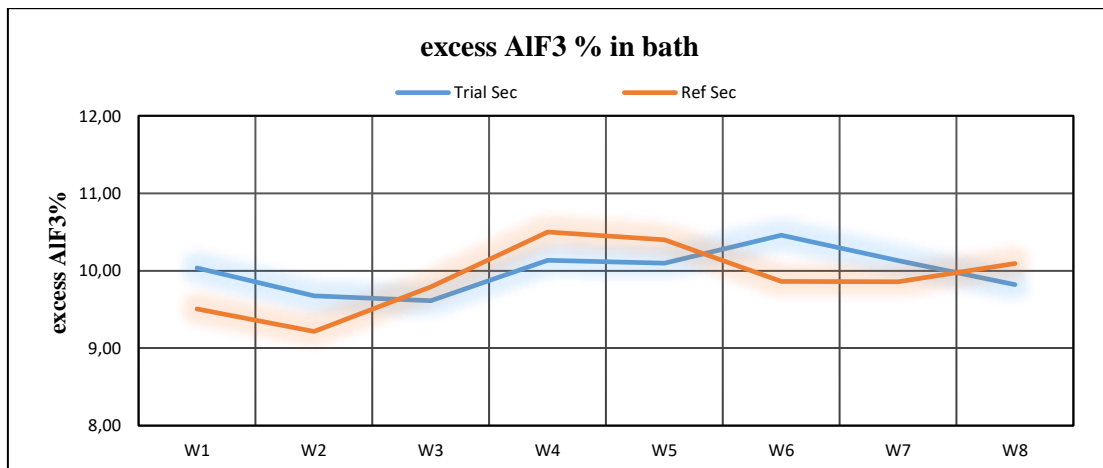


Figure 19. Average excess AIF3 weekly trend (Sec = Section).

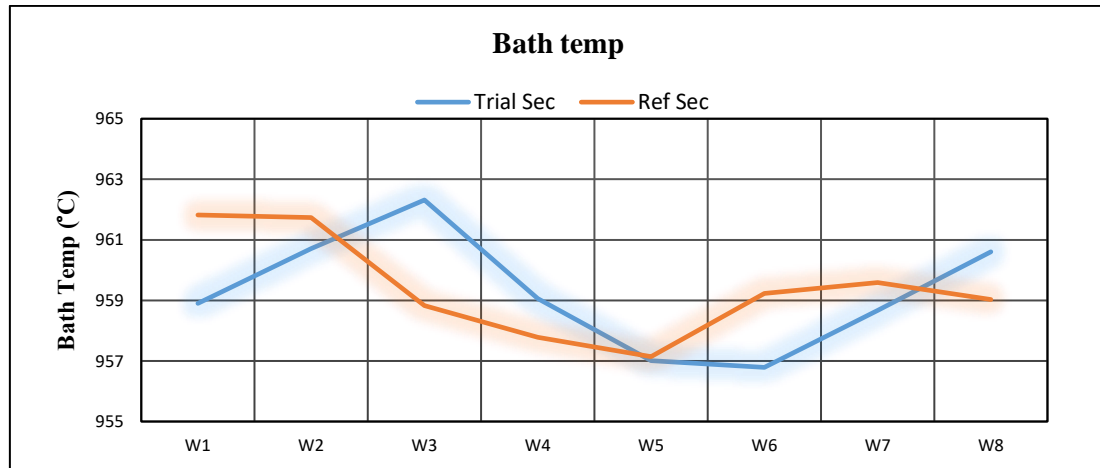


Figure 20. Average bath temperature weekly trend (Sec = Section).

4. Conclusions

We conclude that the use of the coating material has the potential to reduce air oxidation and net carbon consumption (NCC), without affecting pot parameters and composition of the butts. There is a butt weight increase of around 15 kg and a top oxidation reduction by 3.1 mm which is equivalent to a NCC reduction of 5-6 kg C/t Al. This NCC reduction in turn reduces the environment impact and thus, is a very cost-effective solution for reduction of carbon footprint. It can be seen from the age-wise study on butt weight and top oxidation, that there is a sharp rise in top oxidation and a sharp decline in butt weight after 10 days, indicating the end of the life of the coating at that stage of the anode life.

Despite the higher average vanadium content in the Plant-2 anode samples, the coating has proved to be effective in reducing the rate of air burn. This coating application also is better than conventional techniques from safety point of view. There is no chance of coating material breaking off even when the anodes bump against each other or during transportation from the rodding shop to the potline. In line with the encouraging results from the lab-scale and bench-scale trials, we are working on automating the coating application process in our rodding shop, with minimal manual intervention and no compromise on the quality of the coating application and the rodding cycle time.

5. References

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