Studies on Influence of Recycled Anode Butts on Properties of Prebaked Anodes used in Aluminium Electrolysis

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Abstract

In the electrolysis process of aluminium, anode butts are recycled and used together with calcined petroleum coke and coal tar pitch for the manufacture of prebaked anodes. The dry aggregate of green anode consists of 25-35 % butts along with various fractions of calcined petroleum coke. The quality of these butts has a strong influence on the properties of the anodes. This paper covers few studies carried out at NALCO (National Aluminium Company Ltd) smelter plant to investigate the effect of quantity and quality of butts on properties of anodes. It has been observed that increased quantity of butts in the anode recipe helps in improvement of mechanical properties of anodes whereas use of improperly cleaned butts and soft butts have a deleterious effect on the reactivity behaviour of anodes.

Keywords: Aluminium electrolysis, Prebaked anodes, Recycled butts

1. Introduction

The Hall-Héroult process used to produce aluminium uses carbon anodes as positive current carriers. These anodes get consumed during the electrolysis process and need to be replaced on a regular basis. For production of one tonne of aluminium metal about 1.95 tonne of alumina and 0.45 tonne of carbon are required. The useful life of an anode inside the electrolytic pot is around 24-25 days. The unconsumed part of anode is called spent anodes or anode butts, which upon removal from the cells are cleaned for removal of adhering bath material. The cleaned butts are further processed for recycling into the carbon making process.

The NALCO smelter plant potlines with a production capacity of 0.46 million tonne aluminium production per annum consists of 960 AP18 technology cells. A direct electrical current 180-185 kA is passed through the electrolyte, entering the cell through prebaked carbon anodes and conducted out of the cell through steel current collector bars that are fixed in the carbon lining. The aluminium oxide is decomposed into aluminium and oxygen. The aluminium metal deposited at the bottom acts as cathode. The oxygen formed then reacts immediately with the carbon anode to form carbon dioxide and carbon monoxide. The overall reaction is represented by the following equation (1) assuming no CO is formed.

$$2Al_2O_3 + 3C = 4Al + 3CO_2 \tag{1}$$

The prebaked anodes are manufactured in the NALCO carbon plant which is equipped with two green anode plants, three anode baking furnaces and two rodding shops. Prebaked anodes of size 1450x1000x550 mm and weight 1185-1190 kg are used in NALCO pots. The anodes are made of 55-65 wt% petroleum coke, 14-17 wt% coal tar pitch and 15-30 wt% recycled anode butts and are replaced on a regular schedule in 72 shifts (24 days) or 76 shifts (25.3 days) depending on anode quality. As per the design of the rodded anodes usually 70-75 wt% of the anodes is consumed and the residual 25-30 wt% of the initial weight of the anodes (butts) are sent to rodding shop for recycling. These anode butts are cleaned of any adhering particles of bath (electrolyte) in the butt cleaning shop, shot blasted, crushed and are then recycled back to green anode plant for the production of new anodes.

(a) **(b)** **(c)**

Figure 1. Images of (a) full anode, (b) anode butt with cover material and (c) cleaned anode butt.

Because the anode butts are re-used, their quality features are of great importance. It is well known that the amount and cleanliness of the butts influence anode physical properties such as the mechanical strength as well as the reactivity behaviour, thus have a strong impact on the properties of the anodes. The quality of butts is dependent on anode quality and performance of anodes during pot operation. It has been ascertained that good butts are hard, have low sodium contents, a high ignition temperature in air and low reactivities in CO_2 and air. Butts of bad quality are soft and very reactive. It was found that when poorly cleaned or soft anode butts are used, the anode quality suffers considerably [1]. The butt quality, quantity used and their influence on the anode quality have been examined and described in this paper.

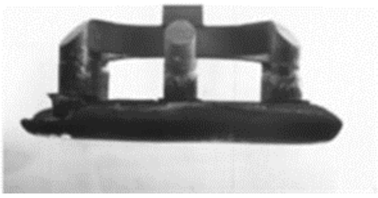
2. Role of Anode Butts in Anode Making Process

Anode butts though recycled back are one of the major raw materials for anode making. All smelters are equipped with butt cleaning and stripping facilities in the rodding shop. Bath material sticking to the butts are removed first and then anodes are shot blasted for removal of residual bath from the surface of the anodes, crushed and recycled back to green anode plant. The ideal butt properties are low sodium content, hard butts, low air and CO_2 reactivity and high ignition temperature [2].

In any aluminium smelter, visual inspection of butts after shot blasting stage provide an indication about

- Anode quality used in the electrolysis process
- Anode behaviour in the electrolysis process
- Anode butt cleaning efficiency

The butt height and weight help in calculation of net carbon consumption, presence of any bath layer on the surface of butts indicate about the cleaning efficiency of shot blasting operation. Increase in sodium level in anodes is attributable mainly to improper cleaning of butts. Effective cleaning of butts ensures low sodium content in anodes. The height of anode butts under the pin help in deciding the shift cycle.




(a) **(b)**

Figure 2. Images of (a) anode butt with pin attack and (b) anode butt with excessive reactivity.

The following studies were carried out in NALCO smelter plant to assess the impact of quality and quantity of recycled butts which are used as one of the important components of anodes:

1. Influence of sodium in butts on anode quality
2. Influence of hardness of butts on anode quality
3. Influence of quantity of butts on anode quality
4. Correlation between butt height and butt weight and net carbon consumption.

3. Experimental Work

3.1 Studies on Influence of Sodium in Butts on Anode Quality

The sodium content in butt particles used in dry aggregate to prepare green anodes and sodium in baked anodes are measured on a regular basis. It has been observed that when sodium in butts is in the range 600-800 ppm, sodium in anodes remain at 400-500 ppm. The sodium level in anodes vary with the sodium content in butts. If the bath, which is a sodium compound i.e. Na_3AlF_6, adhering on the surface of the butts is not cleaned properly in the rodding shop, bath particles get carried away along with crushed butts and make their way to green anode body. Anode core samples from different lots of baked anode production were collected from the plant and analyzed for sodium content and same anode core samples were used to conduct the tests of carboxy reactivity of anodes and air reactivity of anodes. Correlations between carboxy reactivity residue of anodes and sodium in anodes is shown in Figure 3. Correlations between air reactivity residue of anodes and sodium in anodes is shown in Figure 4.

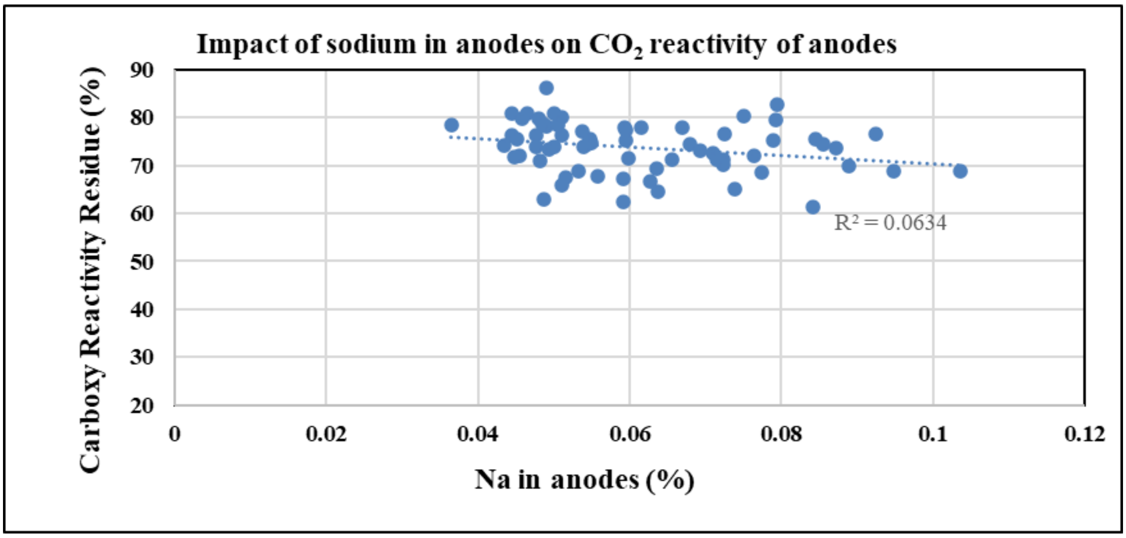


Figure 3. Impact of sodium in anodes on CO_2 reactivity of anodes.

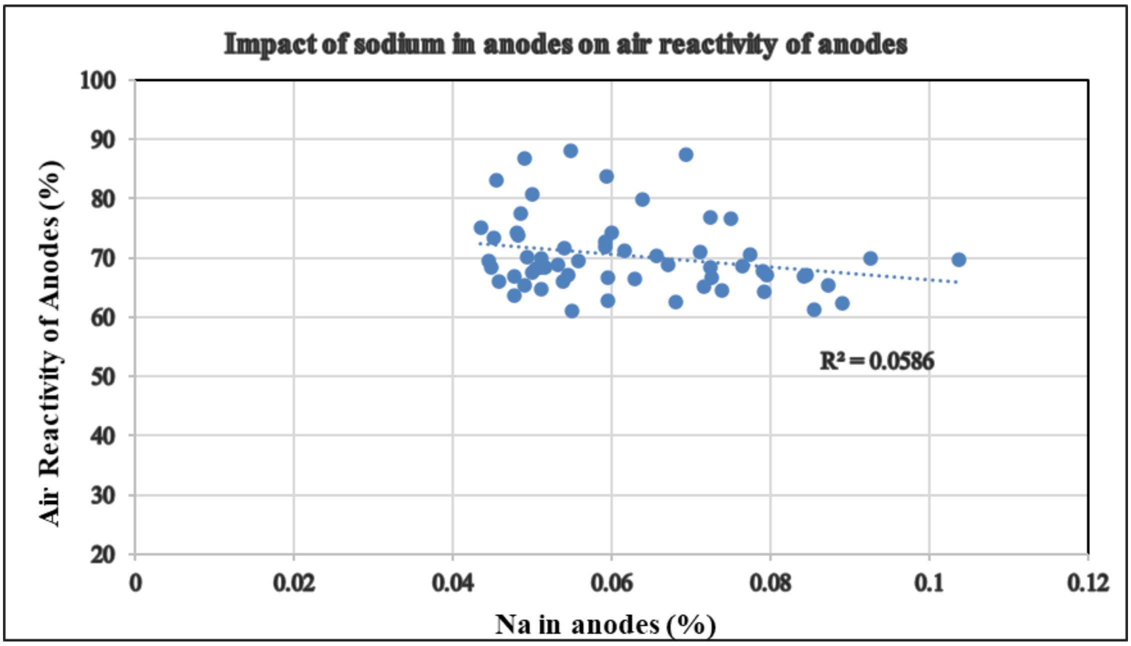


Figure 4. Impact of sodium in anodes on air reactivity of anodes.

It can be observed from Figure 3 that CO_2 reactivity of anodes (indicated by carboxy reactivity residue values) decrease with increase in sodium level in anodes. The correlation is weak due to influence of other parameters affecting CO_2 reactivity e.g. baking level, sulfur in anodes etc. Similarly, from Figure 4 it is observed that air reactivity of anodes (indicated by air reactivity residue values) also decrease with increase in sodium level in anodes. Here also correlation is weak due to influence of vanadium in anodes.

3.2 Studies on Hardness of Butts and its Influence on Anode Quality

Depending upon the behaviour of anodes in the pots and the anode quality used, butts are diagnosed as hard butts or soft butts. Usually most of the butts removed from the electrolysis process are hard butts. However, there is always slow impregnation of sodium from bath into anodes. Moreover, in case of half fallen/full fallen anodes, sodium formed at the negatively charged anode piece (during cathodic contact) quickly diffuses into the carbon due to rapid Na into carbon intercalation. Sometimes this leads to high sodium impregnation of anodes. Impregnation of carbon anodes leading to soft butts can also occur when there is too small interpolar distance (pinch effect), carbon lumps in bath under the anode, clad failure, anode spikes etc. The use of soft butts/impregnated butts influence the burning behaviour of anodes and create, due to a vicious circle, softer and softer butts and an extreme amount of carbon dusting in the electrolysis pots. Carbon dusting increases bath resistivity leading to high volt/pot, high temp, reduced current efficiency and increased net carbon consumption. In such a catastrophic situation, both a daily skimming of the pots and a complete stoppage of butts addition to the anode recipe may be required [3].

The recycling of one single impregnated butt contributes to the sodium contamination of anodes as much as 30 normal butts. Fully impregnated butts may have 1-3 % Na. These impregnated butts when recycled to anodes, increase permeability, anode burn off and hence increased net carbon consumption during electrolysis.

To study the influence of hardness of butts generated in the smelter potlines of NALCO, hardness was measured in 500 spent anodes using butt hardness tester (RDC 188, R&D Carbon Switzerland) after cleaning of butts through shot blasting machine. The hardness of butts is depicted as the penetration depth of the RDC188 hardness tester probe in millimetres (mm). The classifications of butt quality are as follows:

Hard butt:	1-3 mm
Medium butt:	4-5 mm
Soft butt:	>6 mm

Measurement results showed 416 butts as hard butt, 74 butts as medium butt, and 4 butts as soft butts. During the inspection of the butts, it was also seen that cases of anode pin exposure was more in medium hardness butts and soft butts. This is one of the reasons of iron contamination in the aluminium metal in electrolytic pots.

Butt hardness figures were correlated with butt height as shown in Figure 5. Bench scale studies were carried out to ascertain the influence of hard butts and soft butts on anode quality, and is presented in Table 1. Anodes made from soft butts have very high sodium i.e., 0.78 % which has affected the carboxy reactivity of anodes and air reactivity of anodes. Carboxy reactivity residue CRR of anodes has decreased by 7.18 % compared to CRR of anodes made from normal butts. Similarly, air reactivity residue is decreasing by 14.78 % in anodes made out of hard butt to as low as 50-56 % in anode made out of soft butt. Reactivity dust figures are also on the higher side. This would lead to excessive carbon dusting inside the pots leading to high resistance in bath layer, increased skimming of carbon dust and due to vicious circle softer and softer butts will be produced.

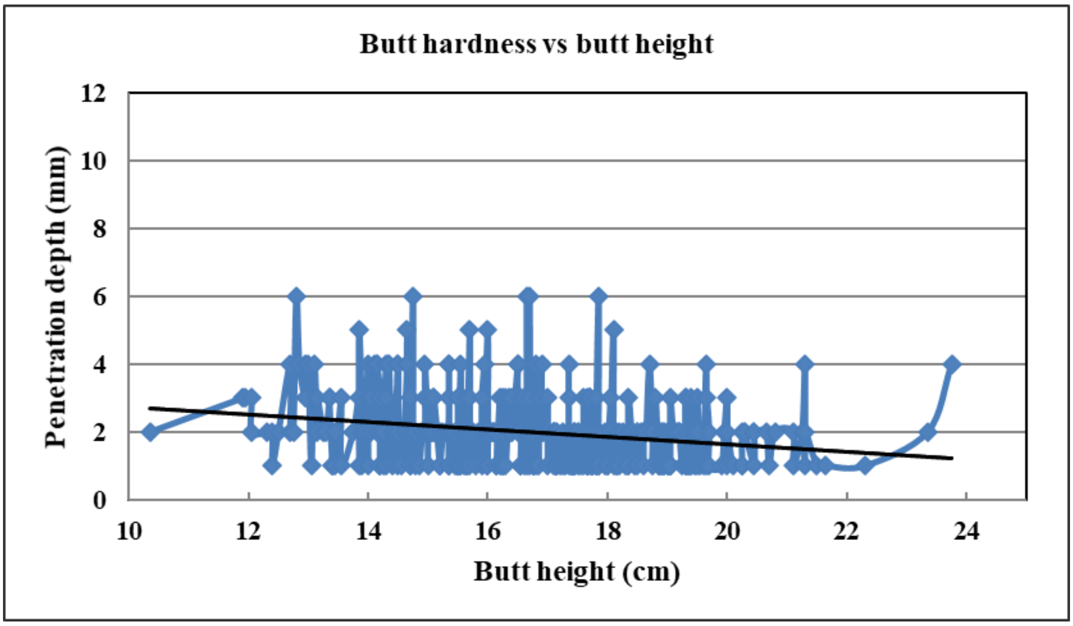


Figure 5. Correlation between anode butt hardness and butt height.

Table 1. Quality of bench scale anodes from Soft and Hard Butt.

Anode Properties	Anodes from hard butts	Anodes from soft butts
Green anode density (g/cm^3)	1.640	1.586
Baked anode density (g/cm^3)	1.578	1.535
Resistivity (μΩm)	73.04	78.0
Air Permeability (nPm)	3.65	5.79
Coefficient of Thermal Expansion CTE 10^{-6} (K^{-1})	4.47	4.61
Carboxy Reactivity Residue (%)	71.98	64.80
Carboxy Reactivity Dust (%)	12.20	18.30
Carboxy Reactivity Loss (%)	15.82	16.91
Air Reactivity Residue (%)	65.07	50.29
Air Reactivity Dust (%)	11.47	18.87
Air Reactivity Loss (%)	23.46	30.84
Na (%)	0.085	0.78

There is a considerable decrease in apparent density of green and baked bench scale anode. Apparent density of green anode is decreasing from 1.64 g/cm^3 to 1.59-1.60 g/cm^3 and apparent density of baked anode is decreasing from 1.57 g/cm^3 to 1.54 g/cm^3

To further study the impact of fully impregnated anodes with pot bath on anode quality, anode butts of half fallen/ fallen anodes were collected from the rodding shop. Quality comparison of bench scale anodes made up of sodium impregnated butts and normal butt is shown in the Table 2.

Table 2. Quality of bench scale anodes made from sodium impregnated butt.

Sample Identification	Anodes from normal butt	Anodes from sodium impregnated butt
Green anode density (g/cm^3)	1.638	1.633
Baked anode density (g/cm^3)	1.574	1.549
Resistivity (μΩm)	69.27	74.90
Air Permiability (nPm)	4.55	4.77
Coefficient of Thermal Expansion CTE 10^{-6} (K^{-1})	4.259	4.48
Carboxy Reactivity Residue (%)	83.87	73.29
Carboxy Reactivity Dust (%)	5.46	9.82
Carboxy Reactivity Loss (%)	10.68	16.89
Air Reactivity Residue (%)	63.71	67.84
Air Reactivity Dust (%)	12.08	7.98
Air Reactivity Loss (%)	24.22	24.17
Na (%)	0.078	0.33

As shown in the Table 2, baked anode density decreases by 0.025 g/cm^3 for anodes made using sodium impregnated butt in comparison to anodes made using normal butt. Resistivity of anodes for sodium impregnated butt increases by 5.62 μΩm. Carboxy reactivity residue (CRR) decreases by 10.58 % in comparison to anodes made using normal butt.

3.3 Influence of Quantity of Butts used in Anode Recipe on Anode Quality

Bench scale anode batches were prepared using varying quantity of butts in anode recipe dry aggregate with constant pitch level and properties of anodes analysed. The results of the experiments are presented in Table 3.

Table 3. Bench scale anode properties with varying quantity of butts in dry aggregate.

Anode properties	40 % butts	37 % butts	35 % butts	33 % butts	30 % butts	27 % butts
Green anode density (g/cm^3)	1.652	1.645	1.640	1.638	1.636	1.616
Baked anode density (g/cm^3)	1.589	1.577	1.578	1.574	1.565	1.545
Baking Loss (%)	3.89	3.95	3.94	4.24	4.43	4.58
Resistivity (µΩm)	68.23	68.81	69.08	69.27	69.51	76.92
Air Permeability (nPm)	2.33	3.69	2.297	4.55	4.49	4.73
Youngs mod dyn (GPa)	5.10	5.4	5.22	5.15	5.25	4.91
Carboxy Reactivity Residue (%)	81.38	82.78	78.06	83.87	83.35	78.05
Carboxy Reactivity Dust (%)	6.59	5.95	8.70	5.46	6.05	8.97
Carboxy Reactivity Loss (%)	12.04	11.27	13.24	10.68	10.60	12.98
Air Reactivity Residue (%)	68.92	65.46	65.64	63.71	62.77	62.67
Air Reactivity Dust (%)	9.28	10.92	9.55	12.08	12.60	12.92
Air Reactivity Loss (%)	21.80	23.62	24.81	24.22	24.62	24.40
Na (%)	0.084	0.079	0.077	0.078	0.076	0.072

It could be observed that baked anode density increases with increase in quantity of butts in anode recipe. This is mainly due to use of less coke in the recipe containing higher amount of butts and difference in particle shape and structure of a coke particle and butt particle. The coke particles generally have larger pores than butt particles [4]. However, the optimum quantity of butt in anode dry aggregate recipe may be kept in the range 35-37 % depending on the level of increase of Na.

3.4 Correlation between Butt Height and Butt Weight

Based on the measurements taken during the experiment, butt height and butt weight were correlated as shown in Figure 6.

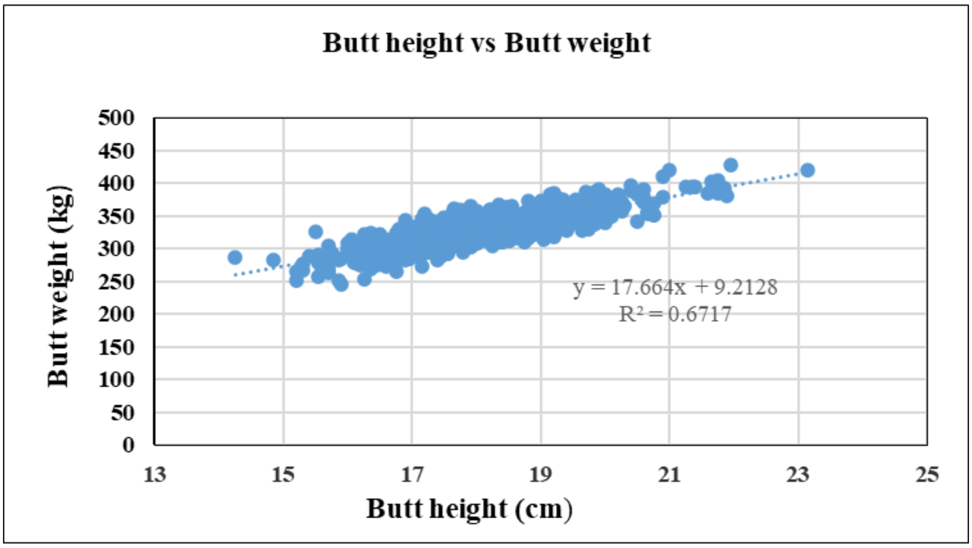


Figure 6. Correlation between butt height and butt weight.

It was observed that the butt weight can be predicted from butt height provided the butts generated have good shape and contour with more than 90% cross-section. However, the height of butts with exposed pins, cracks, excessive reactivity cannot be considered for the butt weight calculations.

From the butt weight data, net carbon consumption was derived for an operating current 185 kA, current efficiency 94 %, anode density 1.54-1.55 g/cm^3 ,assuming constant normalised baked anode weight and anode life 24 days with 16 anodes in one pot, as shown in Figure 7.

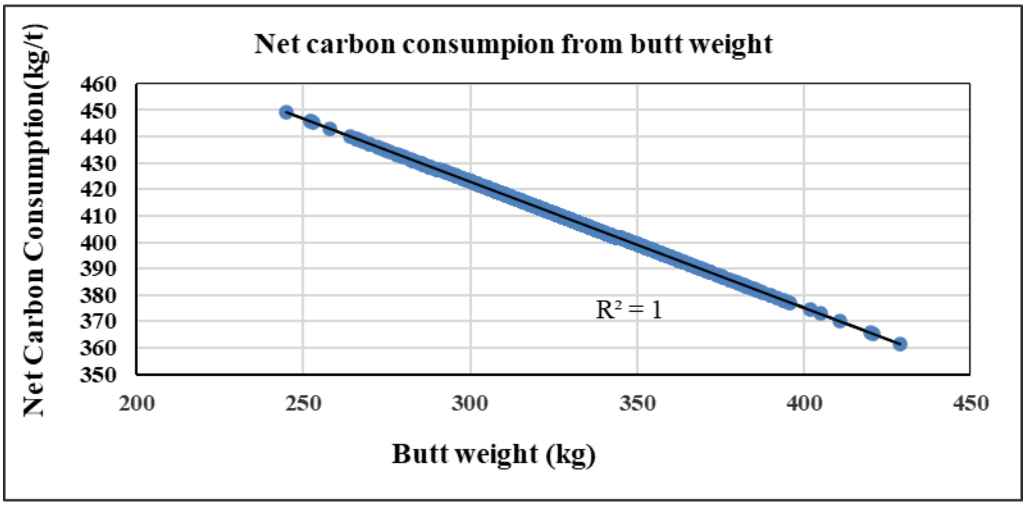


Figure 7. Correlation between butt weight and net carbon consumption.

It can be seen from the graph in Figure 7 that net carbon consumption kg C/tonne aluminium metal can be predicted theoretically from the measured butt weight in this manner and actions can be taken to improve the same.

4. Ongoing R&D Work – System Improvement

An inline automated butt inspection system developed by R&D has been installed in one rodding shop of carbon plant for continuous monitoring and analysis of anode butt parameters. The data e.g., butt height, butt weight, presence of bath on the surface of butts, carbon under the pin is recorded on a continuous basis.

5. Conclusions

From the studies carried out on the influence of quality and quantity of butts on anode properties, the following conclusions can be made:

i) Quality and quantity of anode butts play a significant role in prebaked anode making process. Good anode quality not only depends upon good quality of raw materials such as calcined petroleum coke, coal tar pitch but also depends upon good butt quality and quantity to be used in anode making.

ii) Butt hardness measurement can be employed as a tool for assessing the quality of butts generated from the electrolysis process. It provides an insight about the performance of anodes used in the electrolysis process so that improvements can be made in the carbon plant process and pot operation parameters.

iii) Carbon plant may maximize recycling of cleaned butts for anode making as increased quantity of butts in anode recipe helps in improvement in mechanical properties of anodes. Only limiting factor to watch for is sodium. Up to 35% anode butts in course fraction of anode dry aggregate can be used safely without affecting any quality parameters of anodes.

iv) Increased sodium in anode butts which could be due to improper cleaning of butts, diffusion of Na from pot bath has a deleterious effect on reactivity behaviour of pots.

v) Soft butts and impregnated butts may be removed from the process loop and discarded as they contain very high level of sodium which has deleterious effect on anode quality and pot operation.

vi) Net carbon consumption can be predicted from butt height and butt weight.

vii) Study results and information presented in this paper would be helpful to smelter plant personnel in understanding the role and importance of anode butts in aluminium electrolysis process.

6. References

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