Improvement in oxidation Behaviour of Prebake anodes used in NALCO smelter plant

Binuta Patra[1] **and Anindya Palchowdhury**[2]
1. Deputy General Manager (Chem)
2. Manager (Mech)
1. NALCO, Bhubaneswar, India
2. NALCO, Angul, India
Corresponding author: binuta.pata@nalcoindia.co.in

Abstract

In view of the importance of the anode carbon consumption on the economics of the Aluminium production process & CO_2 emission, great efforts have been made in recent years to study the problem. The excess carbon consumption due to air oxidation is mainly affected by the metallic impurities e.g. vanadium, nickel, sulphur present in the raw materials and calcium, sodium in recycled butts. Detailed studies have been carried out at NALCO Smelter Plant to understand the problem of excess anode carbon consumption during the electrolysis process .Experiments were carried out in laboratory scale, bench scale and plant scale by addition of boric acid in green anode recipe. The result of the one year plant level trial is presented in this paper. It could be established that there is significant improvement in air reactivity residue figures of anodes by addition of boric acid.

Keywords: Prebaked anodes, Air reactivity, boric acid.

1. Introduction

Aluminium is produced conventionally by the Hall Heroult process, by the electrolysis of alumina dissolved in cryolite containing molten electrolytes at temperatures around 955-960 deg C. In these Hall Heroult cells, the anodes are usually prebaked carbon blocks which are electrochemically consumed.

Prebaked anodes are made of a mixture of calcined petroleum coke and coal tar pitch. Production of these anodes involves various unit operations including preparing & treating the starting materials, metering, preheating, mixing, forming and baking at high temperature & then rodding for enabling the current supply to the pot.

The overall chemical reaction in the aluminium production is summarized as in equation (1)

$$2Al_2O_{3(dissolved)}+3C_{(solid)} \rightarrow 4Al_{(liquid)}+3CO_{2\,(gas)} \qquad (1)$$

The theoretical consumption of carbon as per the reaction is 334 kg per one ton of aluminium produced. However the actual carbon consumption is 400-450 kg per ton of aluminium produced.

The extra carbon consumption is affected by the current efficiency of pots and various secondary reactions occurring during the process such as:

- Oxidising reaction with oxygen from air on the upper part of anodes if the anodes are not protected.
- Carbon oxidation reactions with CO_2 at the surface of the anode bottom immerse in liquid bath.
- Selective oxidation of binder pitch coke.

The carbon consumed accounts for 20-25% of Aluminium production cost.

Various additives have been tried to improve the oxidation resistance of anodes. The addition of phosphorous has been found beneficial in reducing the oxidation losses but phosphorus contamination in aluminium metal lowers the current efficiency. AlF_3 & Alumina have also been tried but have been found not very beneficial as far as overall improvement in oxidation behaviour of anodes. Protective coatings have also been proposed, notable a layer of aluminium on anode surfaces. Poor wet ability of carbon by the aluminium leads to problems in the uniformity of such coatings. Another proposed coating consists of alumina, but this has the disadvantage of creating thermal insulation around the anode leading to local overheating and acceleration of oxidation process.

Boron compounds in the form of B_2O_3 & H_3BO_3 have been found to inhibit the catalytic impurities by forming stable alloys therewith. Attempts to coat the anodes with Boron compounds have not been successful. As per US patent 3852 107 coating of 1-5 mm thick coating has been tried on the anode surface by spraying. Another attempt was made to coat the carbon body with a solution of ammonium pentoborate or ammonium tetraborate. This method was also unsuccessful. Later an impregnation method has been somewhat successful where the anode surface up to a certain height is immersed into a solution containing boron compounds.

Attempts have been made by NALCO R&D department to carry out experiments and plant trials by addition of Boric acid (H_3BO_3) in anodes.

2. Background

Calcined petroleum coke (CPC) has been used for more than 120 years to produce the carbon anodes used in the Hall-Heroult aluminium electrolysis process. Prebaked anodes are produced with 55–65% CPC, 13–15% coal tar pitch binder, and 20–30% recycled anode butts. The anodes are consumed at a net consumption rate of approximately 400 - 450kg carbon/ton aluminium for modern smelting cells. CPC is produced by heating or calcining green petroleum coke (GPC) at temperatures greater than 1200 degC. The production of GPC has remained essentially the same since 1929 when the modern delayed coking process was born. This was followed in 1935 by the development of the rotary kiln calcining process, which is the most commonly used technology in the Western world. The aluminium industry has had a ready supply of good-quality GPC and CPC for many years, but the situation has become more challenging over the last 10-15 years due to a general trend toward higher impurity levels resulting from changes in crude and refining economics.

The general trend has been an increase in trace metals like V and Ni and an increase in S levels.

The quality of CPC being supplied to NALCO differs mainly in apparent density & metallic impurities which is again dependant on the quality of green petroleum coke used in the calcining plant. High Vanadium in CPC affects the air reactivity of anodes and current efficiency of pots. Several technical papers have been published on this subject which explains the impact of changes in CPC quality on anode quality and smelter plant operation performance. Vanadium level in NALCO’s CPC supplies vary in the range 0.002 to 0.025% Due to high vanadium levels in CPC, the air reactivity residue of anodes remains at the level of 60-65%.

Hence R&D dept has made this endeavour to find an adaptable method for improvement of air reactivity of anodes and made a trial at plant level to show the actual benefits.

3. Consumption of Anode carbon

In the electrolysis process the removal of oxygen evolved from the dissolution of alumina in the high temperature molten cryolite electrolyte, necessitates that carbon anode is consumed according to the stoichiometric reaction as shown in equation (1) at a theoretical rate of 334kgCarbon/T Aluminium. Typical current efficiencies of 90% & above, side reactions of carbon under the pot conditions raise this figure to 400-450 kg Carbon/T of metal.

The overall carbon consumption is the combined effect of electrochemical consumption, chemical consumption and physical anode consumption.

3.1 Electrochemical consumption

At the cell current densities 0.7-1.2 A/cm^2 the production of Carbon Dioxide according to the equation (1) is favoured.

At low current densities (0.1-0.3 A/cm^2) the thermodynamically favoured product for the reaction between carbon and oxygen is shown in equation (2)

$$Al_2O_{3\ dissolved}+3C_{\ solid} \rightarrow 2Al_{\ liquid}+3CO_{\ gas} \qquad (2)$$

In practice however the operating plants report anode consumption as a function of metal production to take into account any current inefficiencies that lead to excess consumption.

3.2 Chemical Consumption

Two major gasification reactions lead to chemical attack of carbon anodes

Reaction of oxygen at the exposed surface of the anode (air burn) is as per equation (3)

$$O_2+C \rightarrow CO_2 \qquad (3)$$

Back reaction of the carbon dioxide produced in the reduction equation with the anode carbon (the Boudouard reaction or carboxy attack) is represented by equation (4)

$$CO_2 + C \rightarrow 2CO \qquad (4)$$

In aluminium electrolysis cells it has been observed that in both the reactions, the reaction rates are temperature dependant and the chemical reaction depends on the distribution of contaminants effective as catalysts or inhibitors, structure of surface, porosity etc. The consumption due to oxidation is mainly affected by the metallic impurities present in the raw materials specially Vanadium, Nickel, Sulphur, calcium and Sodium in recycled butts.

It has been found out that the most significant coke impurities for air burn reactivity are vanadium, sulphur, nickel and sodium. For the carboxy reaction it is concluded that sodium is the most important impurity to consider. In the absence of sodium other impurities may be detrimental to anode behaviour.

3.3. Physical anode consumption

Physical consumption due to selective oxidation of the binder phase with associated physical losses of the coke matrix (a process known as dusting) can occur leading to carbon consumption. The differential reactivity of the binder coke and filler aggregate leads to selective gasification of binder phase, weakening the bond structure and resulting in coke particles either becoming detached or removed by mechanical, thermal or magnetic forces. This is referred to as dusting and can be seen as loose carbon particles floating on top of the bath that has not been electrolytically consumed.

3.4 Overall anode consumption

Overall carbon consumption is the combined effect of electrochemical consumption, chemical consumption and physical consumption of anodes.

Gjorthem and Welch (1988) have given the contribution of various carbon loss mechanisms to the overall consumption [13] as shown in Table 1

Table 1. Overall anode carbon consumption.

Reaction	Conc. Range (%theoret.)		Kg C/kg Al (94% CE)
	Min.	Max.	
Electrochemical CO_2	99.8	98.5	0.353-0.350
Electrochemical CO	0.8	2.0	0.002-0.005
Pore reaction CO_2	4.0	8.0	0.014-0.028
Airburn	8.0	20.0	0.028-0.075
Dusting	0.4	4.0	0.002-0.014
TOTAL	113	132.5	0.394-0.468

The losses due to carboxy reactivity, air reactivity and dusting represent the excess consumption that has the potential to be reduced by improving the quality of carbon anode. Anode consumption mechanism is shown in Fig 1 & Fig 2.

Plant consumption figures have often been correlated with various anode properties in order to try and identify the important parameters. Fischer et al. (1991) gave the following formula [1] based on the continuous monitoring of anode properties and anode consumption during twenty years, shown in equation (5)

$$NC = C + 334/CE + 1.2(BT - 960) - 1.7CRR + 9.3AP + 8TC - 1.5ARR \quad (5)$$

where:		
	NC	net consumption, kg C / ton Al
	C	cell factor
	CE	current efficiency, %
	BT	bath temperature, ^{0}C
	CRR	carboxy reactivity residue, %
	AP	air permeability, nPm
	TC	thermal conductivity, W / m K
	ARR	air reactivity residue, %

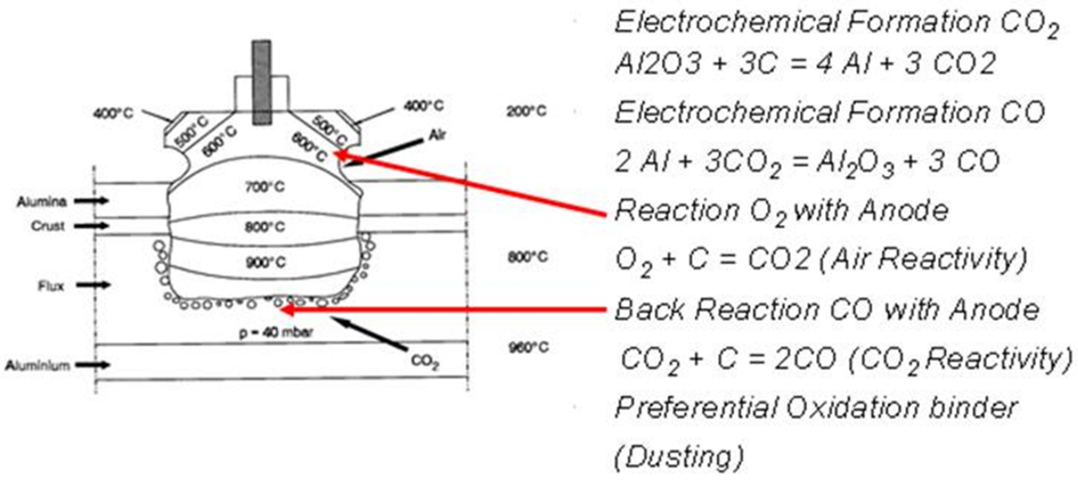

Figure 1. Anode consumption mechanism in the pot.

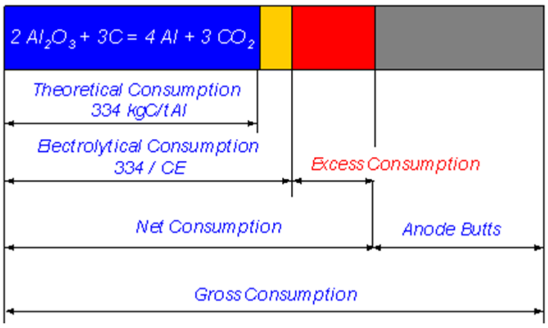

Figure 2. Carbon consumption.

4.0 Impact of impurities in CPC on reactivity of anodes

The impurities Vanadium, Nickel, Na & Sulphur have considerable influence on the air reactivity of coke & thereby anodes. The ignition temperature of CPC is affected by these impurities.

For a CPC of average structure & porosity the regression equation from statistical analysis [12] is given below in equation (6)

$$T(\text{ignition}) = 1/\ln(1.0012 + 1.5 \times 10^{-7}\ \text{Na}/\text{S} + 1.14 \times 10^{-7}\ \text{V}) \qquad (6)$$

where: T(ignition) Ignition temperature, K
Na Sodium content, ppm
S Sulphur content, %
V Vanadium content, ppm

Correlations obtained on anodes from a study carried out at NALCO smelter plant are given below in Figure 3, Figure 4 & Figure 5.

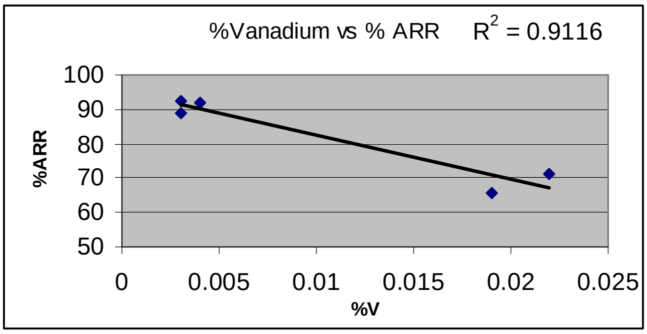

Figure 3. Correlation between Vanadium in CPC and Air reactivity Residue of anodes.

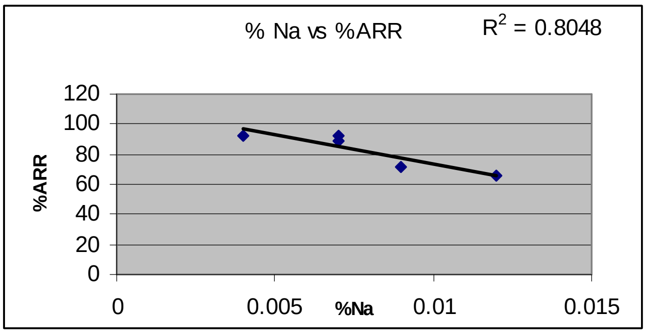

Figure 4. Correlation between Sodium in CPC and Air reactivity Residue of anodes.

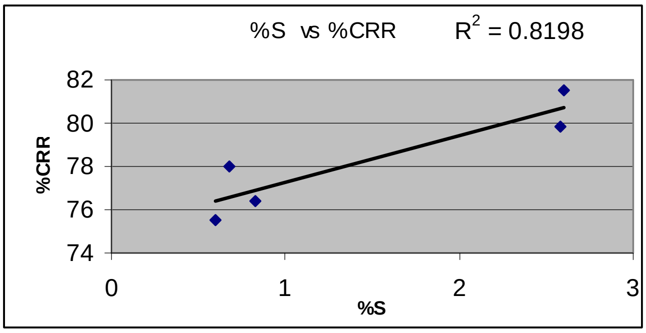

Figure 5. Correlation between Sulphur in CPC and Carboxy Reactivity Residue of anodes.

5.0 Plant Parameters

Smelter plant of National Aluminium Company Ltd (NALCO), is located at the city, Angul in the state of Odisha, India and has an installed capacity of 4.6 million tons of aluminium (NALCO) per year. The smelter has 960 electrolytic cells in four AP18 potlines, The AP18 Electrolytic cells use prebake carbon anodes, manufactured in two captive carbon plants. There are two green anode paste plants, three baking furnaces and two rodding plants operating on latest technologies.

The characteristics of the CPCs used and for manufacturing green and baked anodes are given in Table 2

Table 2. Typical characteristics of calcined petroleum cokes (CPCs) used in smelter plant.

PARAMETERS	Source of supply				
	I	II	III	IV	V
Apparent Density(gm/cc)	1.756	1.75	1.72	1.72	1.72
Real Density (gm/cc)	2.069	2.07	2.062	2.07	2.06
Moisture (%)	0.05	0.02	0.06	0.04	0.01
Ash (%)	0.07	0.18	0.38	0.17	0.31
Fe (%)	0.012	0.008	0.038	0.033	0.019
Si (%)	0.016	0.035	0.031	0.025	0.022
S (%)	0.680	0.828	0.60	2.602	2.580
Ni (%)	0.003	0.003	0.012	0.015	0.019
V (%)	0.004	0.003	0.020	0.022	0.019
Na (%)	0.004	0.007	0.007	0.009	0.012
Ca (%)	0.006	0.005	0.012	0.007	0.012
HGI	40	38	38	39	34
+ 4.75mm size (%)	38.5	38.5	34.8	34.2	32
-0.3 mm size (%)	4.5	8.4	6.3	8.5	6.7
Grain Stability (%)	74	75	64	74	70
CO2 Reactivity (%)	14.2	15	21.4	11.2	21.4
Air Reactivity (%/min)	0.06	0.05	0.29	0.16	0.13

6. Previous work done in laboratory scale, bench scale & plant scale

Laboratory scale, bench scale & plant scale trials have been carried out at Smelter R&D successfully by addition of boric acid in the anode matrix. Results of the studies are given below

6.1 Laboratory scale & bench scale studies

Anode bench scale plant facility & anode core testing equipment supplied by R&D Carbon Ltd, Switzerland were used for the experiments. Results are tabulated in Table3.

Table 3. Bench scale trial results of bench scale anodes.

Anode properties	**Before addition of boric acid**	**After 0.1 to 0.2% boric acid addition in anode**
Air reactivity residue ARR (%)	64.01	97.6
Air reactivity loss ARL (%)	21.99	2.32
Air reactivity dust ARD (%)	14.11	0.040
Carboxy reactivity residue CRR (%)	80.65	92.32
Carboxy reactivity loss CRL (%)	11.88	5.73
Carboxy reactivity dust CRD (%)	7.45	1.93

6.2 Plant scale trial in one section of Potline3

Trial was carried out in 15 test pots and 15 reference pots in Potline 3 of smelter plant for a period of 5 anode change cycle. CPC sourced from a single supplier was used during the entire experimental period. 0.2-0.3% of boric acid was added in green anode plant. Results of anode core tests and pot parameters are tabulated in Table 4 & Table 5.

Table 4. Plant scale trial in one section of potline - results of anode core samples.

Anode properties	**Normal anodes used in reference pots**	**Boric acid treated anodes used in test pots**
Air reactivity residue ARR (%)	67.19	93.41
Air reactivity loss ARL (%)	22.22	6.57
Air reactivity dust ARD (%)	10.59	0 .02
Carboxy reactivity residue CRR (%)	74.46	92.08
Carboxy reactivity loss CRL (%)	15.95	6.42
Carboxy reactivity dust CRD (%)	9.59	1.50
Green anode density (gm/cc)	1.610	1.608
Baked anode density(gm/cc)	1.551	1.546
Resistivity (micro-ohm mtr)	54.54	54.44
Flexural Strength (MPa)	11.45	12.37
Thermal conductivity (W/mk)	3.30	3.31
Air Permeability (nPm)	1.813	1.785
Coeff of Thermal expansion(10-6 K^{-1})	4.299	4.043

Table 5. Results of Pot Line.

Parameters	**Reference Pots**	**Test Pots**
Metal production (Kg/pot/day)	1385.37	1389.9
Current Efficiency (%)	93.66	93.97
Average Butt Height (cm)	17.43	18.14
Average Baked Anode Weight (kg)	1167.79	1161.73
Average Butt Weight (kg)	306.37	326.73
Average Carbon Consumption (72 Shift)/anode (Kg)	861.42	835
Total Carbon Consumption in 72 shift / pot (Kg)	13782.72	13360
Average Carbon consumed/Pot/Day (Kg)	574.28	556.67
Net carbon Consumption (kg/T)	414.53	400.51
Avg Titanium as Ti (%)	0.004	0.001
Avg Vanadium as V (%)	0.012	0.005
Avg Boron as B (%)	0.002	0.007
Avg Iron as Fe (%)	0.160	0.156
Avg Silicon as Si (%)	0.066	0.065

7. One year large scale plant trial

For the purpose of one year large scale plant trial, GAP-2 was selected as the boric acid charging location. Boric acid charging has been carried out regularly in all the shifts it varied between 0.07 and 0.1%.

7.1 Tests & measurements

7.1.1 Impurities in CP coke

CPC samples were collected at regular intervals from green anode plant and analysed for impurities. Test results are given in Table 6.

Table 6. Impurities in CP Coke.

Impurity	**Range**
Iron as Fe (%)	0.015-0.034
Silicon as Si (%)	0.021-0.037
Nickel as Ni (%)	0.007-0.022
Vanadium as V (%)	0.011-0.023
Sulphur as S (%)	1.35-3.32
Sodium as Na (%)	0.005-0.011
Calcium as Ca (%)	0.006-0.011

7.1.2. Butt height & weight measurement

Butt weight and butt height of sample butts were measured during the trial period. Improvement in butt height and butt weight was observed in boric acid treated anodes as shown in Table 7 & Table 8

Table 7. Butt height measurement results.

	Butt height (cm)
Before experiment	18.75
During experiment	19.375
Increase	0.625

Table 8. Butt weight measurement results.

	Butt weight (Ton)
Before experiment	0.3163
During experiment	0.3235
Increase	0.0072

7.1.3 Metal analysis

Aluminium metal samples collected during the trial period were analysed for various impurities mainly to see the increase of boron content in the metal. Test results are given in Table 9.

Table 9. Aluminium metal analysis from pot line.

Month	**Fe (%)**	**Ti (%)**	**V (%)**	**B (%)**
Mar'16	0.1660	0.0046	0.0109	0.0022
Apr'16	0.1399	0.0024	0.0090	0.0028
May'16	0.1580	0.0052	0.0117	0.0032
June'16	0.1986	0.0028	0.0104	0.0030
July'16	0.1423	0.0017	0.0090	0.0035
Aug'16	0.1829	0.0017	0.0116	0.0035
Sept'16	0.1510	0.0021	0.0116	0.0036
Oct'16	0.1490	0.0023	0.0138	0.0041
Nov'16	0.1577	0.0020	0.0107	0.0031
Dec'16	0.1682	0.0021	0.0109	0.0030
Jan'17	0.1577	0.0025	0.0097	0.0029
Feb'17	0.1607	0.0013	0.0093	0.0036
Mar'17	0.1584	0.0026	0.0125	0.0029

7.1.4 Anode quality measurement

Anode core samples were collected during the experiment from anode baking furnaces ABFII & ABF III and analysed for important properties as shown in Table 10 and Table 11.

Table 10. Anode quality measurement data of ABF II.

Anode Quality	**Before addition of boric acid**	**After addition of boric acid**
Vanadium as V (%)	0.015	0.016
Sulphur as S (%)	1.993	2.07
Air reactivity residue ARR (%)	62.96	83.48
Air reactivity dust ARD (%)	10.2	3.16
Air reactivity Loss ARL (%)	26.82	13.35
Carboxy reactivity Residue CRR (%)	80.53	82.85
Craboxy reactivity dust CRD (%)	6.64	6.32
Carboxy reactivity Loss CRL (%)	12.84	10.83
Air permeability AP (npm)	1.28	1.52
Thermal Conductivity TC W/mK	3.94	3.73
Lc (deg A)	30.88	29.76

Table 11. Anode quality measurement data of ABF III.

Anode Quality	**Before addition of boric acid**	**After addition of boric acid**
Vanadium as V (%)	0.018	0.016
Sulphur as S (%)	2.14	2.09
Air reactivity residue ARR (%)	60.15	86.84
Air reactivity dust ARD (%)	13.03	2.15
Air reactivity Loss ARL (%)	26.82	11.01
Carboxy reactivity Residue CRR (%)	80.8	80.9
Craboxy reactivity dust CRD (%)	7.81	7.2
Carboxy reactivity Loss CRL (%)	11.36	11.91
Air permeability AP (npm)	1.32	1.74
Thermal Conductivity TC W/mK	3.91	3.58
Lc (deg A)	30.49	29.54

Table12. Results of one year plant scale trial

	Before experiment	**After experiment**	**Difference**
Air reactivity residue ARR (%)	61.6	85.2	+23.6
Air reactivity dust ARD (%)	11.6	2.7	-8.9
Boron in metal (%)	0.0022	0.0033	+0.0011

8. Results & Discussion

Improvement in air reactivity residue (ARR) of GAP-2 anodes and reduction in air reactivity dust has been observed after start of boric acid addition in Mar’16. Boron content in aluminium metal has increased by only 11 ppm. The results of the trial are summarized below in Table 12.

9. Conclusion

It has been observed from the above trials carried out at smelter plant of NALCO that boric acid addition in anodes leads to improvement mainly the air reactivity residue of anodes, this will help in reduction of net carbon consumption keeping the boron content of metal within acceptable limits. Simultaneously there will be a reduction of greenhouse gas (CO_2) emission and thus carbon footprint of smelter plant. Air reactivity dust of anodes has also decreased by 8.9%. This will help in lowering the carbon dust and mushroom generation in the pots and thus improvement in current efficiency of pots.

Many aluminium smelters in the world are facing the problem of deteriorating CPC quality mainly due to increased levels of Vanadium, Nickel & Sulphur. The solution enumerated in this paper can be adapted in any smelter for lowering the air reactivity of anodes.

10. References

1. W.K.Fischer, F.Keller and R.Perruchoud, Interdependance between anode net consumption and pot design, pot operating parameters and anode performance. *Light metal 1991 page 681-686*
2. S.M.Hume, R.C.Perruchoud and W.K.Fischer, Gas reactivity testing of raw materials and anodes used in the aluminium industry, *JOM Feb 1994, pages27-31*
3. W.K.Fischer, F.Keller, R.C.Perruchoud, S.Oldlerbolz, Baking parameters and the resulting anode quality, *Light Metal 1993, pages683-694*
4. Zeno de mori, Practical experience with a formula for the prediction of the anode net consumption, *Original publication Light metal 1993*
5. F.Keller, W.K.Fischer, Development of anode quality criteria by statistical evaluation of operational results in the electrolysis. *Light Metal 1982 Pages 729-740*
6. Jeffery G. Rolle and Yen K Hoang, Studies of the Impact of Vanadium and Sodium on the Air Reactivity of Coke and Anodes, *Light Metals 1995, pp 741-745.*
7. Franz Vogt, Ken Ries and Mark Smith, Anode Desulfurization in Baking, *Light Metals1995 pp 691-700.*
8. Hameed Abbas, Khalil Khaji and Daniel Sulaiman, Desulphurization Control during Baking: Its Impact on Anode Performance and Operational Cost ALBA’s Experience, *Light Metals 2010, pp 1011*
9. C. Dreyer, Anode Reactivity: Influence of the Baking Process, *Light Metals 1989, pp 595-602*
10. Christian Dreyer, Bernard Samanos and Franz Vogt, Coke Calcination Levels and Aluminum Anode Quality, *Light Metals 1996, pp 535-542.*
11. Binuta Patra, R.K.Barik, Studies on impact of quality of c.p.coke from different sources on anode quality.*Light metal 2012,pp 1213-1217*
12. S.M.Hume, W.K.Fischer, R.C.Perruchoud, B.Welch, A Model for Petroleum Coke Reactivity. *Light metal 1993*
13. K. Grjotheim and B.J. Welch, Aluminum Smelter Technology—*A Pure and Applied Approach, 2nd edition* (Dusseldorf, Germany: Aluminum-Verlag Publishers, 1988).