Light Metals 2012 *Edited by: Carlos E. Suarez*
TMS (The Minerals, Metals & Materials Society), 2012

STUDIES ON THE IMPACT OF CALCINED PETROLEUM COKE FROM DIFFERENT SOURCES ON ANODE QUALITY

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Keywords: Calcined petroleum coke, prebaked anodes, blending

Abstract

Calcined petroleum coke (CPC) is a major raw material for smelting anodes. The anode quality plays an important role in the smelter productivity and profitability. Since the beginning, the CPC from different Indian suppliers has been used in National Aluminium Company Ltd.

This paper presents the quality of CPC from different sources and their influence on anode quality. Anode bench scale studies have also been carried out by blending CPC from different sources and assessment of anode quality.

Introduction

All aluminium smelters who produce prebaked anodes for aluminium electrolysis are continually seeking to improve anode quality in order to improve the efficiency of smelting operation. It has been observed in our plant, that there is a lot of variation in anode properties. One of the reasons for this was found to be the quality of CPC used for manufacture of anodes. In our plant we depend on many suppliers for providing us CPC.

A bench scale study was carried out with the aim of highlighting the effect of each property of CPC on anode quality. Due to the usefulness of the results obtained this bench scale experiment was followed by plant scale trial.

To further assess whether blending of such cokes would result in any improvement in results, another set of bench scale experiment was carried out by blending different qualities of CPC.

Anode Manufacturing

Typical prebaked anodes for aluminium production contain 60-65% CPC, 14-15 % coal tar pitch (CTP) & 20-25 % recycled anode butts.

The anode manufacturing process involves the following major steps

- Preparation of dry aggregate consisting of various fractions of CPC and having different particle sizes & recycled anode butts by crushing, sieving, grinding & weighting
- Preheating the dry aggregate
- Mixing the dry aggregate with CTP in a mixer
- Vibrocompacting or pressing the green paste to form anode blocks
- Baking the green anodes in refractory lined bake ovens by indirect heating through heavy furnace oil or flue gas following a regulated fire cycle

Anode Quality

In order to obtain an optimum aluminium cells operation, it is crucial to manufacture high quality anodes. Some requirements and effects on cell operation are shown in Table I.

Table-I. Important Anode quality requirements

Quality requirement	Effect
High density & low permeability	Higher anode cycle, lower anode consumption, less carbon dusting
High resistance to oxidation	To minimize the excess of consumption
Sufficient mechanical strength	Structural integrity & handling
Low specific electrical resistivity	Less power consumption
Low impurities	To minimize carbon consumption & contamination of aluminium
High thermal shock resistance	Less cell disruption & anode failures

Quality of CPC used in NALCO

Most of the CPC properties have a direct impact on anode quality and anode performance in the electrolysis process.

The quality of CPC being supplied to NALCO mainly differs in apparent density & metallic impurities which depends on the quality of green petroleum coke used in the calcining plant. The calciners in the North Eastern region of India are integrated to the crude oil refineries. The green coke is a by-product of these refineries. The quality of petroleum coke obtained from the Indian crude is very good in terms of apparent density & metallic impurities. However the sulphur content is low & calcium is sometimes high. These two impurities have a negative impact on the carboxy reactivity of anodes.

Whereas there are other calciners who mostly blend the local and imported green/raw petroleum coke before processing in the calciner. The quality of CPC from such calciners may vary considerably. Generally the imported green cokes contain more sulphur, vanadium and nickel and lower bulk density when compared to local source.

In order to determine the impact of different CPC on the anode quality, a bench scale study and some trials in smelting operation were performed. The outcome of these studies is presented below.

Anode Bench Scale Experiment

The bench scale study was carried out using CPC from different suppliers. The analysis results of CPC are presented in Table II and that of anodes are presented in Table-III.

Table-II. Analysis of CPC from different sources

Parameters	Sample Identification				
Samples	S1	S2	S3	S4	S5
Apparent density(Hg) g/cm^3	1.756	1.75	1.72	1.72	1.72
Real density g/cm^3	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	0.003	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
Size (+ 4.75mm) %	38.5	38.5	34.8	34.2	32
Size (-0.3 mm) %	4.5	8.4	6.3	8.5	6.7
Grain stability %	74	75	64	74	70
Carboxy reactivity %	14.2	15	21.4	11.2	21.4
Air reactivity % /min	0.06	0.05	0.29	0.16	0.13

Procedure

1. Recipe as adopted in Green Anode Plant (GAP) was prepared using pilot sieve shaker & air jet collision mill
2. 20 bench scale anodes (100mm height & 50mm dia.) were prepared using R&D Carbon equipment RDC-161
3. Green anodes were baked in bench scale anode baking furnace RDC 166 up to 1100°C
4. Anode cores were analyzed using R&D Carbon testing equipments, XRay Diffractometer, Helium Pycnometer & XRay Fluorescence Spectrometer

Bench scale Results

Table –III. Properties of bench scale anodes made out of different types of CPC

Properties	Unit	S1	S2	S3	S4	S5
Green anode density	g/cm^3	1.654	1.648	1.586	1.614	1.619
Baked anode density	g/cm^3	1.557	1.553	1.504	1.52	1.525
Air reactivity Residue	%	92.1	92.34	89.1	71.4	65.65
Air reactivity loss	%	7.6	6.73	9.5	20.4	23.05
Air reactivity dust	%	0.3	0.93	1.3	8.2	11.29
Carboxy reactivity residue	%	78	76.39	75.5	81.5	79.86
Carboxy reactivity loss	%	12	12.82	12.3	11.7	12.92
Carboxy reactivity dust	%	10	10.79	12.2	6.8	7.22
Na	%	0.010	0.010	0.026	0.034	0.035
Lc	Å	29.2	30.0	29.3	30.2	31.0
Real density	g/cm^3	2.089	2.09	2.087	2.089	2.083

Results

The influence of the major parameters of CPC on important properties of bench scale anodes are discussed below.

Impact of apparent density of CPC on Green & Baked anode density: The anode density will be affected by different CPC apparent densities. Higher the coke density higher is the anode density.

Impact of impurities in CPC on Air reactivity of anodes: It may be observed that anodes manufactured with CPC from S1 & S2 have higher air reactivity residue compared to the anodes with S3, S5 & S4. This may be explained by the amount of impurities in coke. Impurities such as vanadium, nickel, sodium & sulphur have considerable influence on the air reactivity of coke & thereby anodes. The ignition temperature of CPC is affected by these impurities.

For CPC of average structure & porosity the regression equation [1] from statistical analysis is

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

Impact of impurities in CPC on Carboxy reactivity of anodes: Anodes using S4 and S5 cokes showed higher carboxy reactivity residue. The sulphur content of these cokes was higher, which increases the carboxy reactivity. The impact of sulphur, calcium and sodium on carboxy reactivity [1] is expressed in the formula below.

Carboxy reactivity (%) of CPC= (4.0 + (0.0411 * Na ppm + 0.101 * Ca ppm))/ S % (2)

Discussions on anode bench scale studies

Anodes produced with S1 and S2 CPC showed higher densities. Some other parameters such as air reactivity residue, air reactivity loss & air reactivity dust values were better due to low vanadium & sodium contents.

Added to that, S1 and S2 coke showed higher carboxy reactivity loss and lower carboxy reactivity residue, due to lower sulphur content in the crude.

Plant Scale Trial

After successful completion of the bench scale experiments a full fledged plant scale trial was carried out by actually using anodes made of different types of cokes in pot line. CPC having wide difference in their properties was chosen for conducting the trial. Quality of two types of CPC is shown in Table-IV.

Table-IV. Analysis of two types of CPC used in the experiment

	AD*	%Fe	%Si	%Ni	%V	%S	%Na	%Ca	HGI*	Size +4.7 mm %
Reference CPC	1.73	0.023	0.023	0.02	0.017	1.44	0.01	0.014	37	34
Test CPC	1.77	0.028	0.023	0.006	0.004	0.77	0.009	0.011	37	40

• AD (Hg Apparent density in g/cm^3)
• HGI (Hard grove grindability index)

Procedure

Test CPC with higher apparent density was kept in Silo3 and reference CPC with lower apparent density was kept in Silo2 of GAP.

1. Green anodes were produced in GAP using test coke of silo 3 and reference coke of silo 2 and identified as test anodes and reference anodes respectively. Green anode plant data is shown in Table V
2. Anode core samples were collected from test & reference baked anodes and analyzed for baked anode quality using R&D carbon testing equipments. Baked anode core sample analysis data is shown in Table V1
3. Pot line trial in GG2 section of Potline-4 started on 27.05.2010 A shift using test anodes in pot no G31 to G45 (test pots) and reference anodes in pot no G46 to G-60 (reference pots)
4. 76 shift anode changing cycle was followed for both test & reference pots
5. Anode weight, butt weight and butt height were measured to monitor the performance of test and reference anodes
6. Trial period was for three anode changing cycles

Table V. Green anode plant data

Average value	Unit	Reference green anodes	Test green anodes	**Difference**
Weight	kg	1244	1254	**+ 10**
Green density	g/cm^3	1.60	1.62	**+0.02**
Dry density	g/cm^3	1.38	1.40	**+0.02**
CTP	%	14.3	13.75	**- 0.55**

Table –VI. Baked Anode quality

Avg values	Unit	Reference baked anodes quality	Test baked anodes quality	**Remarks**
Baked density	g/cm^3	1.544	1.570	**+0.026**
Resistivity	micro ohm m	55.72	54.51	**-1.21**
Air reactivity residue	%	71.01	91.08	**+20.07**
Air reactivity loss	%	17.42	7.74	**- 9.68**
Air reactivity dust	%	11.57	1.18	**-10.39**
Carboxy reactivity residue	%	76.10	73.76	**-2.34**
Carboxy reactivity loss	%	14.72	14.11	**-0.61**
Carboxy reactivity dust	%	9.18	12.13	**+ 2.95**

Summary of results of trial in pot line

Net carbon consumption per ton of hot metal was estimated during plant scale trial by measuring the baked anode weight, butt weight and the quantity of metal produced in test and reference pots. Summary of performance of test and reference anodes in pot line is tabulated in Table-VII.

Table –VII. Performance of reference and test anodes

Measurement data	Unit	Performance of reference anodes	Performance of test anodes	Difference
Butt Height	cm	16.28	18.32	2.04
Anode Weight	kg	1179	1194	15
Butt Weight	kg	265	315	50
Net Carbon consumption	**Kg carbon/T**	**443.25**	**426.39**	**-16.86**

Discussions of results from plant scale trial

1. There is an increase of green anode density of test anodes by 0.02 g/cm^3 and baked anode density by 0.026 g/cm^3.
2. There is an increase of green anode weight of anodes made from test coke by 10 kg/anode compared to anodes made from reference coke which would result in increased baked anode weight. This increased weight would help in extra shift operation of anodes in the pots.
3. There is a decrease in consumption of CTP for test anodes by 0.55 % compared to reference anodes.
4. There is a decrease of baked anode resistivity of test anodes by 1.21 micro-ohm-m compared to reference anodes.
5. A decrease of net carbon consumption 16.86 kg carbon/T of hot metal is observed due to use of better coke (test coke).
6. An increase of 2 cm butt height is observed with a test coke density of 1.77 g/cm^3. This correspondence to provision of carbon for approx. 4 shifts consumption. Again the advantage of increased butt height decreases with decrease in density of CPC.

Anode Bench Scale Trial on Blending

A trial has been conducted using Anode Bench scale facilities to achieve the desired quality of CPC by blending two types of CPC. Here we have tried to use the fines fraction of both types in the matrix. Simultaneously we also blended 30% of better quality coke in all fractions for comparison purpose.

Sampling

Representative CPC samples were drawn from two types of coke (B1 and B2) having following properties as shown in Table-VIII.

Table –VIII. Analysis of two types of CPC used in the experiment

Properties	**B1**	**B2**
Apparent density (Hg) g/cm^3	1.75	1.72
Real Density	2.08	2.06
Moisture %	0.02	0.01
Ash %	0.18	0.31
Fe %	0.008	0.019
Si %	0.035	0.022
S%	0.828	2.580
Ni%	0.003	0.019
V%	0.003	0.019
Na %	0.007	0.012
Ca %	0.005	0.012
HGI	38	34.00
Size + 4.75 mm %	38.5	32.00
Size -0.3 mm %	8.4	6.7
Grain stability %	75	70
Carboxy reactivity %	15	21.4
Air reactivity % /min	0.05	0.13

Preparation of recipe

The samples were sieved and ground using standard methods. Coarse & Medium fractions were obtained after sieving. Fines fraction was prepared from the coarse & medium fraction. Very coarse fraction & other baked product were taken from the butts sample collected from the plant.

Total 5 experiments were carried out:

1. Recipe from B1 coke (AB1)
2. Recipe from B2 coke (AB2)
3. Recipe prepared by taking the whole of fines fraction prepared from B1coke & rest from B2 coke (AB3)
4. Recipe prepared by taking the whole of fines fraction prepared from B2 coke & rest from B1 coke (AB4)
5. Recipe prepared by adding 30% of B1 coke in all fractions of B2 coke (AB5)

Anode production

Five batches of bench scale anodes were produced from the recipe of each type of CPC. The core samples were analyzed for all the properties. Results are given in the Table-IX.

Table –IX. Anode quality of blending experiment.

Properties	Unit	AB1	AB2	AB3	AB4	AB5
Green anode density	g/cm^3	1.641	1.619	1.625	1.633	1.647
Baked anode density	g/cm^3	1.564	1.525	1.535	1.537	1.546
Air reactivity Residue	%	90.81	65.65	85.44	71.95	69
Air reactivity loss	%	8.71	23.05	12.89	16.57	19.9
Air reactivity dust	%	0.48	11.29	1.67	11.48	11.1
Carboxy reactivity residue	%	73.25	79.86	83.94	72.74	81
Carboxy reactivity loss	%	13.98	12.92	9.56	15.75	11.9
Carboxy reactivity dust	%	12.77	7.22	6.5	11.51	7.11

Discussion of results

AB3 anodes using the fines produced from high grade coke in fines fraction of recipe have better properties than AB2 anodes made from B2 coke. Air reactivity residue has increased from 65.65 % to 85.44%, carboxy reactivity residue has increased from 79.86% to 83.94 %. Carboxy reactivity of AB3 anodes is also better than AB1 anodes as expected.

AB4 anodes using the fines produced from B2 coke in fines fraction of recipe whereas coarse & medium are from B1coke. In this case the anode quality is not as good as that of AB3 & AB5 anodes.

AB5 anodes blending 30% of high grade coke in all fractions of B2 coke has also shown improved properties compared to anodes made from B2 coke. These anodes have higher density (increase of .02 g/cm^3). Additionally, there is an increase in Air reactivity residue from 65.65 % to 69%.

Conclusion

Anode quality and anode performance in pot line can be significantly improved if better quality CPC is used in any Aluminium Smelter Plant. Reduced net carbon consumption will turn into smelting costs savings.

Through the experiments it is shown that there is a direct correlation between apparent density of CPC and apparent density of anodes. Air reactivity of anodes is greatly affected by the presence of vanadium and sodium in CPC. Sulphur in CPC influences the carboxy reactivity of anodes.

Anode bench scale experiments carried out by blending two types of coke having wide difference in properties show that quality of anodes can be improved considerably by blending of fines fraction as well as all fractions. Blending can be adapted by plants which receive CPC with widely different properties. There is also a possibility that CPC calciners blend their green coke to supply consistent quality of CPC to smelter plants.

Acknowledgement

Authors are grateful to NALCO management for granting permission for publishing this paper. Authors are also thankful to all their colleagues in smelter plant who have rendered support for successful completion of plant scale trials. Authors would also like to make special mention of all testing and bench scale facilities provided by R&D Carbon Ltd, Switzerland.

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