Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

FACTORS INFLUENCING BAKED ANODE PROPERTIES

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Keywords: Baked Anode, C.P.Coke, Desulphurization, Baking Temperature

Abstract

EMAL is a primary aluminium smelter with an annual production capacity of 1.32 million tonnes of aluminium. It has 756 cells operating at 385 kA and 444 cells operating at 450 kA. The prebake carbon anodes required for the operation of these cells are produced in two captive carbon plants. For its anode production, EMAL procures calcined petroleum coke from multiple sources. The properties of baked anodes produced during the last two years were analyzed to find correlations between baked anode properties with coke characteristics and process parameters. The analysis show that baked anode properties and anode performance are influenced by raw material properties and process parameters. The understanding gained through the analyses helps in adjusting the process parameters and selection/blending of cokes to produce optimum quality baked anodes that perform well in the cells.

Introduction

Emirates Aluminium (EMAL), located at Al Taweelah near Abu Dhabi in the United Arab Emirates has an installed capacity of 1.32 million tons of aluminium per year. EMAL smelter has 1200 electrolytic cells, of which 756 DX cells operate at 385 kA and the other 444 DX+ cells operate at 450 kA line current. The electrolytic cells use prebake carbon anodes, manufactured in two captive carbon plants

Table 1: Carbon anodes supply to reduction lines.

Parameter	Unit	Lines 1 &2	Line 3
Anode length	mm	1630	1795
Anode width	mm	685	720
Anode weight	kg	1165	1265
Stub holes	No	3	4
Anodes/cell	No	36	36
Anode life in cell	No.of 8-hr shifts	80	80
Anodes required	No. per day	1020	600

The paste plants, baking kilns and rodding plants have latest state-of-the-art technologies for green anode manufacturing, baking of green anodes, sealing of baked anodes and processing of butts.

Several papers have been published describing influence of raw materials properties and the process parameters of green and baked anodes manufacturing on the baked anode properties [1, 2, and 3].

This paper presents a study of the correlations between baked anode properties and raw material properties and process parameters of green anode manufacturing and baking of green anodes, based on EMAL data. The data used covers two years period from August 2012 to July 2014. The raw material analysis, process data from paste plant, baking kiln historians and the core sample laboratory analysis have been used in the study.

Raw Materials and Processes

The carbon anodes supplied to reduction cells are expected to have:

- Good apparent density
- Low electrical resistivity
- High resistance to thermal shock
- Mechanical strength
- Minimum chemical reactivity
- High chemical purity
- Zero physical defects

EMAL's carbon plants use mainly calcined petroleum cokes from calciners located in China, Kuwait, India and South America. The CP cokes from China are calcined in vertical shaft kilns, while the CP cokes from other sources are calcined in rotary kilns. Table 2 shows the physical and chemical properties of CP cokes used in EMAL.

Table 2: Analysis of C P Cokes used in EMAL

Analysis	Unit	Coke A	Coke B	Coke C	Coke D	Coke E
Fe	%	0.014	0.014	0.009	0.007	0.015
Si	%	0.014	0.016	0.003	0.001	0.012
S	%	2.57	2.48	0.62	1.05	2.61
V	%	0.024	0.025	0.024	0.005	0.024
Ni	%	0.022	0.021	0.018	0.008	0.017
Ca	%	0.013	0.013	0.003	0.001	0.006
Na	%	0.006	0.006	0.003	0.004	0.004
Ash	%	0.19	0.21	0.11	0.05	0.17
Moisture	%	0.06	0.08	0.09	0.08	0.07
RD	g/cc	2.081	2.076	2.066	2.072	2.08
VBD	g/cc	0.938	0.945	0.906	0.925	0.888
VM	%	0.4	0.44	0.42	0.44	0.39
HGI		31.5	31.3	34	36	33.8
+ 4 Mesh	%	36.3	36.3	41	27.4	35.7
- 20 Mesh	%	24.6	27	19.4	26.1	22.1
CO_2 Reactivity	%	12.2	11.4	8.6	7	7.9
Air Reactivity	% / min	0.29	0.18	0.16	0.07	0.1
Electrical Resistivity	μΩ.m	464.4	481.7	457.8	441.5	450.3
L_c	A^0	30.9	29.7	27.7	28.8	30.6

The CP cokes (A & B, Table 2) from vertical shaft kiln calciners have higher vibrated bulk density (VBD) as compared to VBD of CP cokes(C,D & E, Table 2) from rotary kiln calciners.

Anodes are produced using blends of cokes, and occasionally from single source cokes. The mix of cokes entering paste plant is crushed and screened to have coarse and medium fractions. The fine fraction is made by grinding coke in vertical mills. The very coarse fraction is prepared from the butts returning from the reduction lines. These four fractions are proportioned and mixed to make the dry aggregate of green anodes. The dry aggregate is preheated, and then mixed with liquid pitch in a continuous mixer to form green paste. The green paste is vibro-compacted under vacuum and top-tool pressure to form green anodes of required dimensions and profiles. The green anodes are baked in open top horizontal flue ring main furnaces using heating equipment with state-of-the- art control logics. The main process and equipment parameters are briefly summarized in Table 3.

Table 3: Main Process and Equipment Parameters

Parameter	Unit	Value
Dry Aggregate GSR	no.	4
Pitch Content	%	12.5-14.5
Mixer Energy	kWh/mt paste	7.5
Vibro-compaction time	sec	45-55
Top tool pressure	bar	4
Vacuum	mbar	25
Baking Temperature	^{0}C	1180-1190

Findings and Discussions

Coke Properties

Vibrated Bulk Density (VBD): EMAL has two coke storage silos each with a capacity of 25,000 tonnes. CP cokes having high VBD are stored in silo A (Table 4) while cokes of normal VBD are stored in the other silo B. Depending on the levels of cokes in silos, the cokes are blended in ratios shown in Table 4.

Table 4: Coke Blending Ratios

Blending	Silo A	Silo B
Ratio 1	100	0
Ratio 2	65	35
Ratio 3	50	50
Ratio 4	35	65
Ratio 5	0	100

Because of blending of cokes in varying proportions, the VBD of the coke mix entering the paste plant varies according to the type of cokes and the blend ratio. The Figures 1 and 2 show correlations found between VBD of coke blends and pitch addition, and between the green anodes dry density with baked anode apparent density. When pitch addition is increased for a given green anode dry aggregate recipe, the anode dry density increases, reaches a peak at a certain value of pitch addition and then drops if pitch addition is increased further. The peak dry density values are considered for correlations.

The dry density (DD) of green anode is calculated from the green anode apparent density (GAD) using the formula:

$$\text{Dry Density} = \text{GAD}\,(1 - \text{Pitch\%}/100)$$

The baked anode apparent density is correlated to the dry density of its green anode.

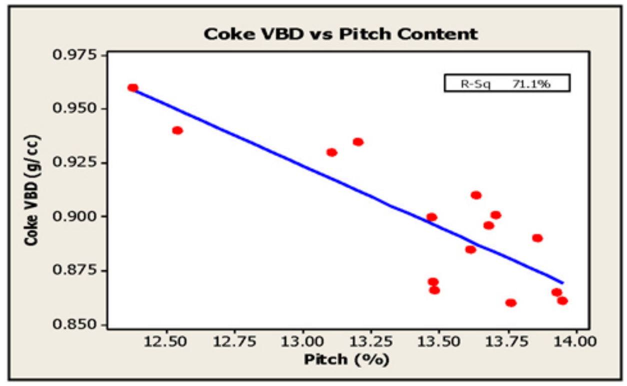

Figure 1:Vibrated Bulk Density of Coke Blends vs. Pitch Addition

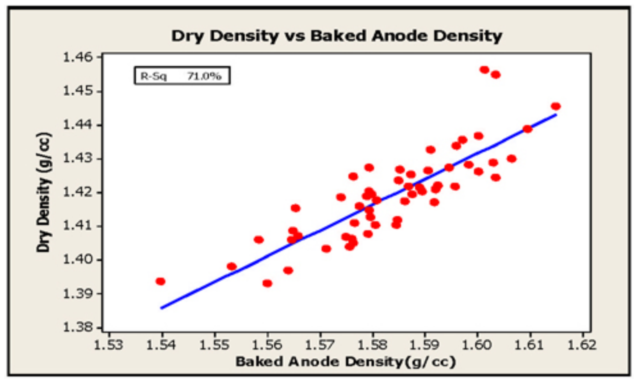

Figure 2: Green Anode Dry Density vs. Baked Anode Apparent Density

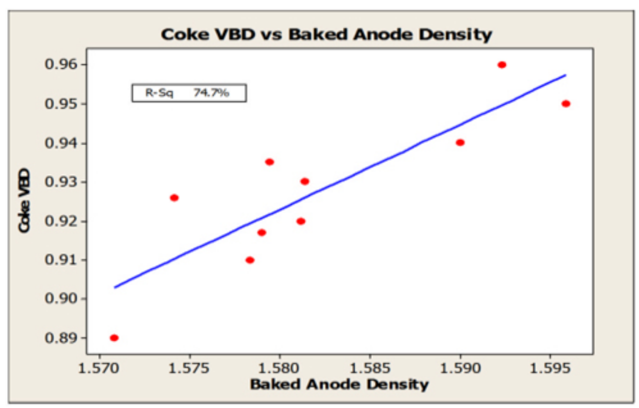

Figure 3: Vibrated Bulk Density of Coke Blends vs. Baked Anode Apparent Density

Figure 3 shows that baked anode density increased with increasing VBD of coke blends.

Sulphur and Elemental Impurity Content: The sulphur content in the CP cokes from most suppliers is in the range of 2.5 – 3.0%. A few CP cokes however have sulphur content of about 1%. It was noticed that high sulphur content cokes also have higher content of elemental impurities, such as silicon, iron, calcium, nickel and sodium (Figure 4).

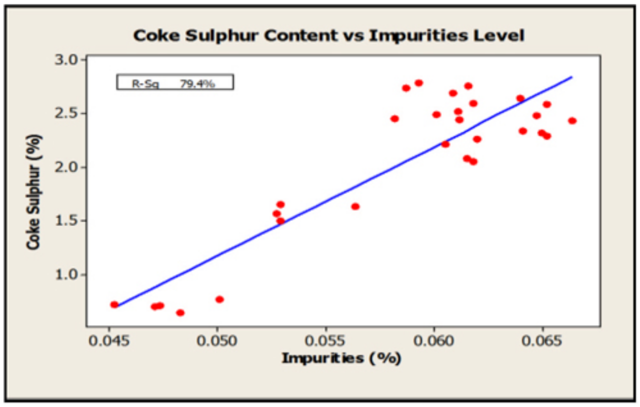

Figure 4: Coke Sulphur Content vs Impurity Content

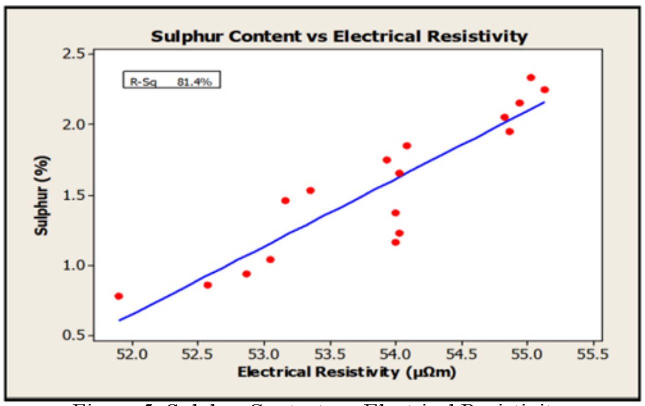

Figure 5: Sulphur Content vs. Electrical Resistivity

Anodes made with high sulphur coke exhibited higher electrical resistivity (Figure 5). As the mix of cokes used has relatively higher VBD (>0.90 g/cm^3), due to use of shaft kiln cokes, the dry aggregate demands lower pitch addition during green anode manufacturing stage. This may be resulting in lesser physical interface between coke particles and pitch, than when more amount of pitch is added. Besides, there is indication that cokes with high sulphur content exhibit higher tendency for desulphurization [4]. These two factors, namely lesser physical interface between coke particles and pitch coke, and higher desulphurization during anode baking may be contributing to increase in electrical resistivity.

Impurities in coke have adverse impact on CO_2 reactivity of anodes. It is known that elemental impurity such as sodium, calcium and iron act as catalyst for the following reaction:

$$CO_2 + C \rightarrow 2CO \qquad (1)$$

The correlation in Figure 6 shows that when the impurity content (Fe + Ca + Na) exceeded 0.065%, there was a sharp drop in the CO_2 reactivity residue. Above 0.065% impurity content, the CO_2 reactivity residue dropped from about 95% to 90% even though sulphur acts as an inhibitor to the above secondary reaction.

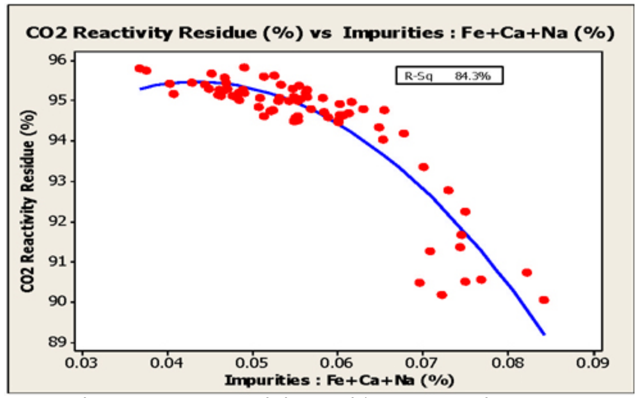

Figure 6: CO_2 Reactivity Residue vs Impurity Content

Paste Plant Parameters

Dry Aggregate Composition: Dry aggregate composition plays an important role in anode performance in cells. In the initial stage of plant operation, the grain to sand ratio (GSR) of anodes was ~ 2. Dry aggregate is characterized by its grain to sand ratio (GSR) which is defined [5] by:

GSR= (% of particles + 0.3 mm) / (% of particles -0.3+ 0.03 mm)

As the line current of cells started moving from 350 kA to 385 kA, there was increase in anode breakage in cells from 0.5 to 2.0 % due to thermal shock. The anode problem is calculated as % of extra anodes supplied against scheduled anode supply to reduction rooms.

Anode Problem (%) = (Extra Anode Supply x 100) / (Scheduled Anode Supply to Reduction Rooms)

The broken anodes had to be replaced with new ones. The anode problem affected the cell operation and increased stress on reduction room operating staff. Investigations carried out to establish the reasons for the increase in anode problem indicated that low grain to sand ratio was the root cause. The anode dry aggregate GSR was increased from 2 to 4. Figure 7 shows the positive impact this had on anode problems.

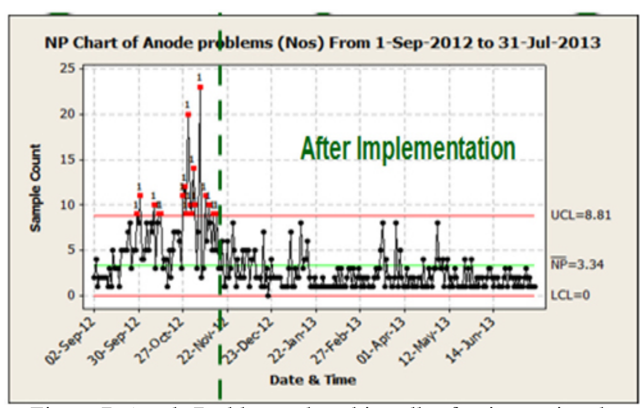

Figure 7: Anode Problem reduced in cells after increasing the GSR of dry aggregate of anodes

Figure 8 indicates the correlation between anode problem and GSR of anodes

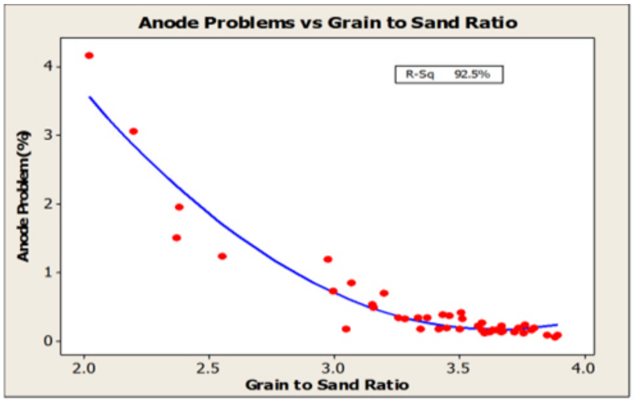

Figure 8: Grain to Sand Ratio vs Anode Problem

Dry density increased with decreasing GSR (Figure 9). A balance between GSR and DD was made to have good baked anode density as well as GSR in the range of 3.5 to 4, to avoid anode cracking in cells due to thermal shock (Figure 8).

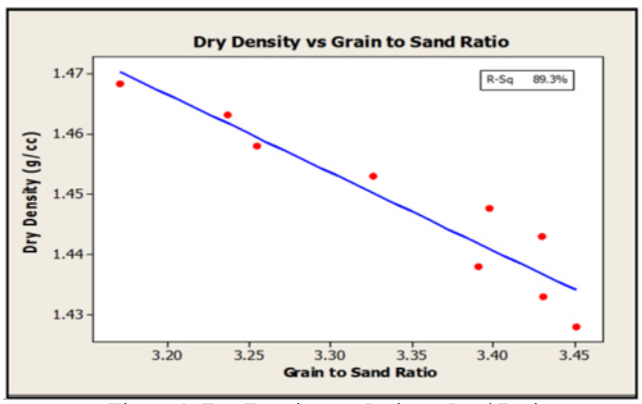

Figure 9: Dry Density vs. Grain to Sand Rati

Mixing Energy: Baked anode density improved from 1.565 to 1.590 g/cm3 as the mixing energy increased from 5.5 to 7.5 kwh/t of paste (Figure 10) for the same blend of cokes and dry aggregate recipe. Mixing energy enables filling of micro pores of coke particles with binder (pitch + ultra-fines). Higher the mixing energy, higher is the effectiveness of filling micro pores with binder as well as coating of coke and butts particles [6].

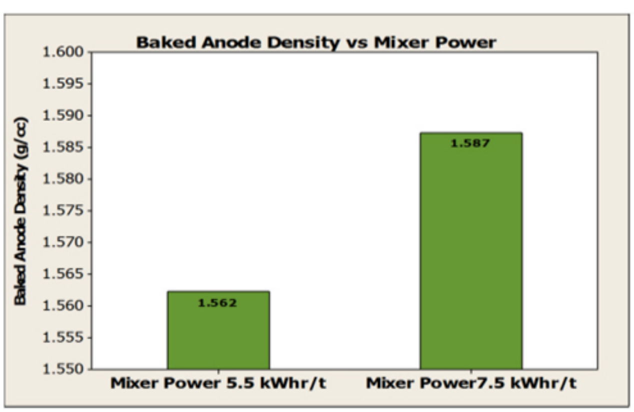

Figure 10: Mixing Energy vs. Baked Anode Apparent Density

Pitch Addition: Pitch addition is optimized to obtain highest green anode dry density for a given blend of cokes and dry aggregate recipe. It was observed that baked anode flexural strength increased with increased pitch addition (Figure 11). Both CO_2 reactivity dust and air reactivity dust decreased with increasing pitch addition (Figures 12, 13). Low reactivity dust is desirable as it helps to keep the carbon dusting under control in the cells.

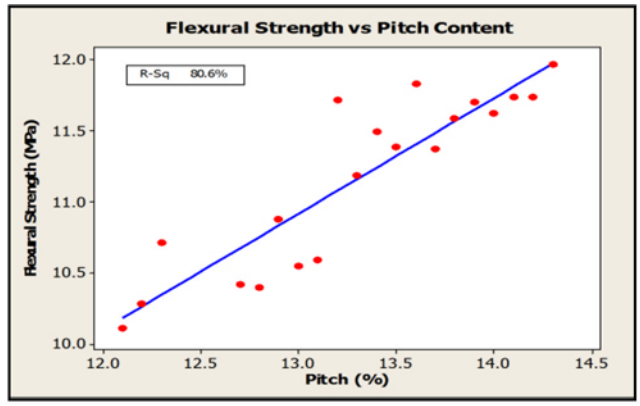

Figure 11: Flexural Strength vs. Pitch Content

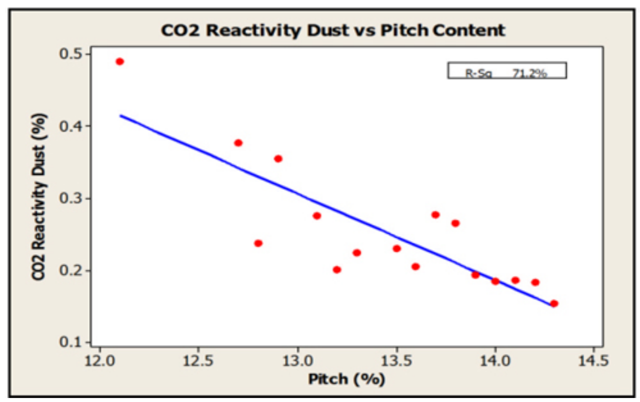

Figure 12: CO_2 Reactivity Dust vs. Pitch Content

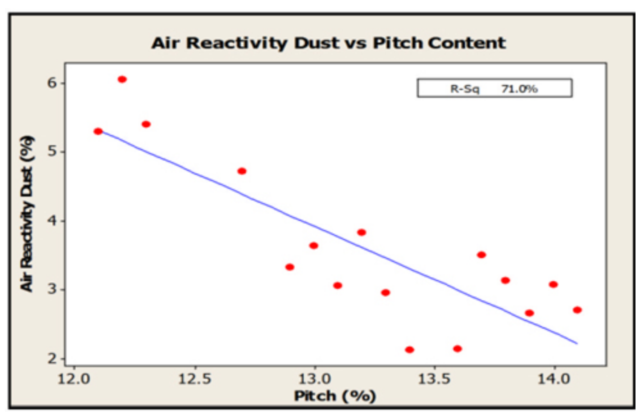

Figure 13: Air Reactivity Dust vs. Pitch Content

Baking Furnace Parameters

Flue Temperature: Baking temperature indicated influence on the following baked anode properties:

- Real density (Figure 14)
- L_c (Figure 15)
- Thermal conductivity (Figure 16) and
- Desulphurization (Figure 17)

Real density, L_c, thermal conductivity and desulphurization of anodes increased with increasing baking temperature. More desulphurization was observed in anodes made of cokes with higher sulphur content (Figure 18). Some cokes desulphurize more readily than others presumably due to differences in structure and sulphur-carbon bonding [4, 7]. It is thought that there is partial disruption of carbon-sulphur bonds during coke calcining. During anode baking, the destabilized carbon-sulphur structure promotes desulphurization.

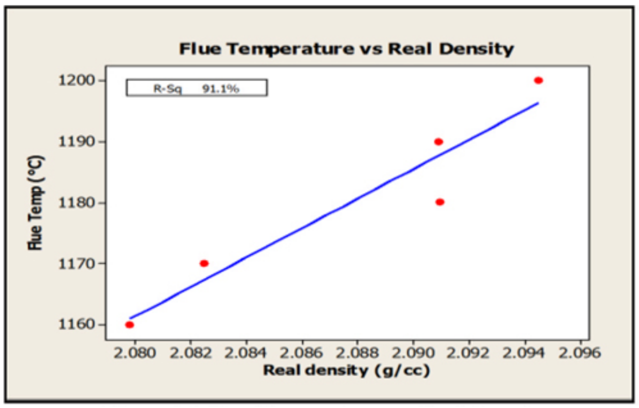

Figure 14: Flue Temperature vs. Real Density

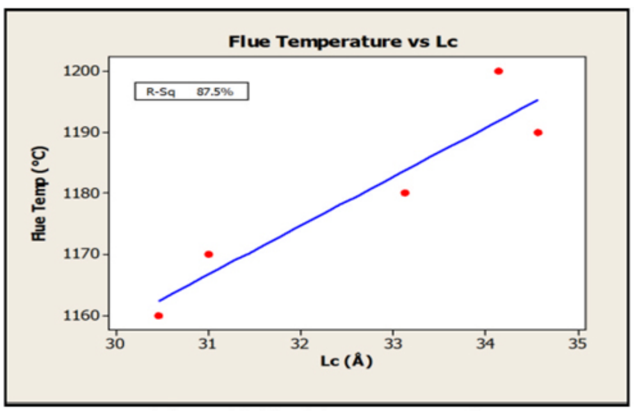

Figure 15: Flue Temperature vs. L_c

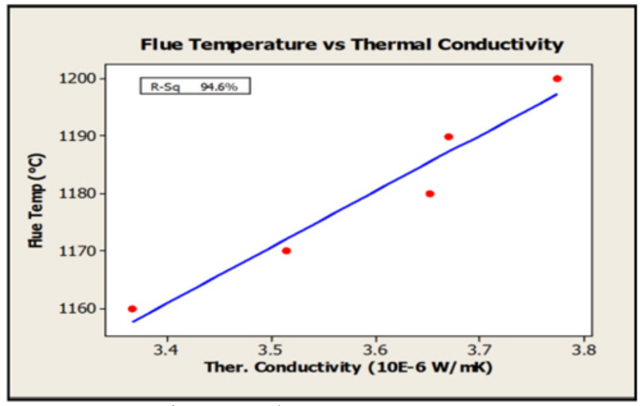

Figure 16: Flue Temperature vs TC

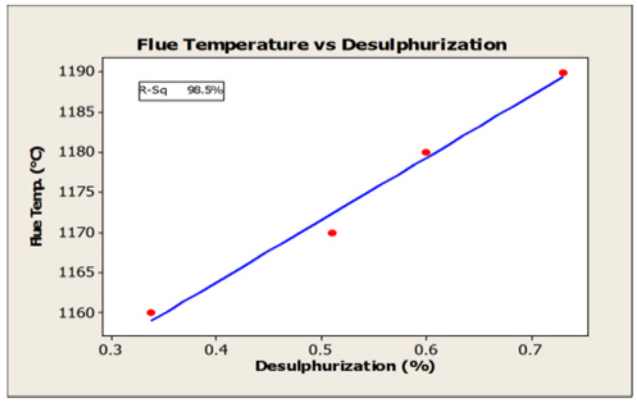

Figure 17: Flue Temperature vs. Desulphurization

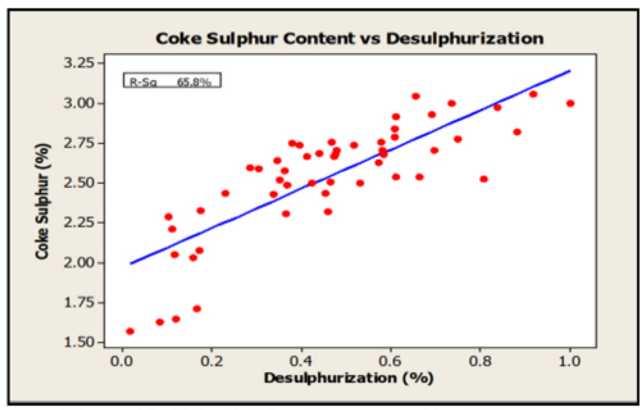

Figure 18: Coke Sulphur Content vs. Desulphurization

Figure 19 shows the adverse impact of desulphurization on the CO_2 reactivity residue of anodes. It is believed that desulphurization creates additional surface within the anode, facilitating increased chemical reaction with CO_2. It is in line with observations reported earlier [8].

The Figure 20 shows that with increase in desulphurization, there is an increase in air permeability. This is indicative of new additional surface being created inside the anode. Desulphurization is detrimental for carbon consumption during electrolysis in cells because it generates new additional surface for the secondary reaction between carbon and CO_2 gas.

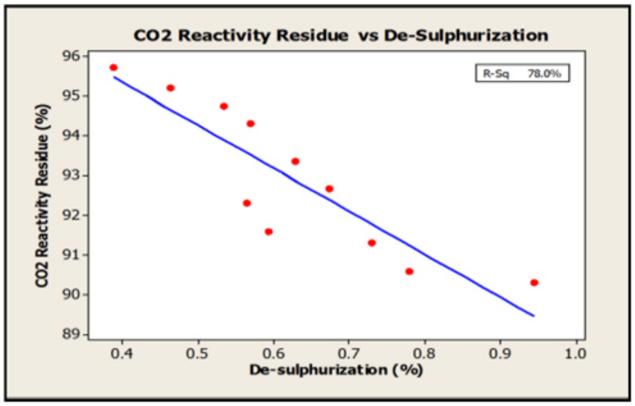

Figure 19: CO_2 Reactivity Residue vs. Desulphurization

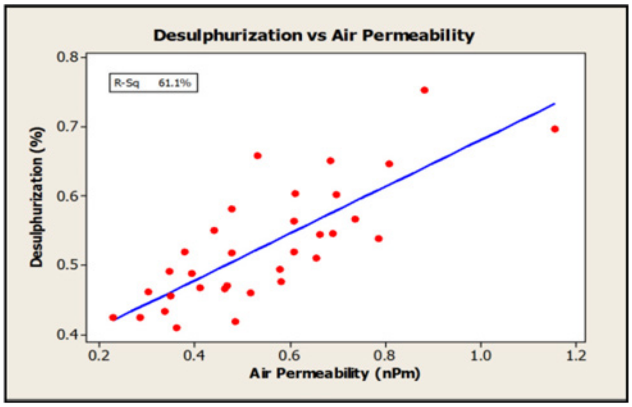

Figure 20: Air Permeability vs. Desulphurization

Figure 21 shows that the air reactivity residue of anodes decreases sharply with increasing vanadium content in coke. Similar observations have been reported [9]. There is trend of increasing vanadium content in cokes with increase in sulphur content. It is necessary to cover the anodes well in cells to minimize air burn and reduce the unnecessary loss of carbon, which otherwise could be used for aluminium production.

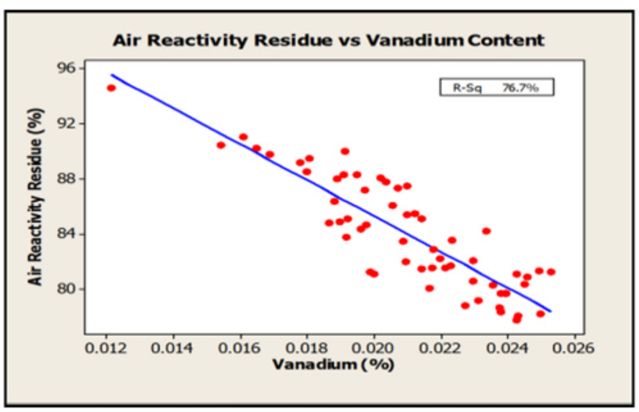

Figure 21: Air Reactivity Dust vs. Vanadium Content

Summary and Conclusions

- Baked anode density increases with VBD of cokes used
- Cokes with high sulphur content also have high content of elemental impurities
- Elemental impurities impact adversely the CO_2 reactivity
- Higher grain to sand ratio (GSR) of dry aggregate gives higher thermal shock resistance to anodes
- Mixing energy has impact on baked anode apparent density
- Anodes with higher pitch content show improved
  - Flexural strength (increases)
  - CO_2 reactivity dust (decreases)
  - Air reactivity dust (decreases)
- Baking temperature has an impact on desulphurization
- Higher sulphur cokes exhibit higher degree of desulphurization
- Desulphurization has adverse impact on
  - CO_2 reactivity
  - Air permeability
- Baking temperature increases
  - Real Density
  - L_c
  - Thermal conductivity
- Vanadium has adverse impact on air reactivity

With the understanding gained above, the process and equipment parameters can be adjusted to produce baked anodes of optimum quality from various coke blends.

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