Role of anode manufacturing processes in net carbon consumption

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Abstract

Carbon anodes are consumed in electrolysis cells during aluminium production. Carbon consumption in pre-bake anode cells is 400 to 450 kg C/t Al, considerably higher than the theoretical consumption of 334 kg C/t Al. This excess carbon consumption is partly due to the anode manufacturing processes. Net carbon consumption over the last three years at Emirates Aluminium (EMAL, also known as Emirates Global Aluminium (EGA) Al Taweelah), was analyzed with respect to anode manufacturing processes/parameters. The analysis indicates a relationship between net carbon consumption and many manufacturing processes, including anode desulphurization during anode baking. Anode desulphurization appears to increase the reaction surface area, thereby helping the Boudouard reaction between carbon and carbon dioxide in the electrolysis zone, as well as reducing the presence of sulphur which could inhibit this reaction. The role of pitch content and elemental impurities in anode and their impact on net carbon consumption were also investigated. The understanding gained through this analysis helped reduce net carbon consumption by adjusting manufacturing processes. For an aluminium smelter producing one million tonnes of aluminium per year, the annual savings could be as much as US $ 0.45 million for every kg reduction in net carbon consumption.

Keywords: Carbon anode; Pitch addition; Anode desulphurization; Net carbon consumption

1. Introduction

Carbon anodes are consumed in Hall-Héroult electrolysis cells during aluminium production. The carbon anode consumption rate is expressed as “net carbon consumption” (NCC) and is a frequently used parameter for evaluating anode performance in reduction cells. NCC in prebake anode cells is in the range of 400 to 450 kg C/t Al. This includes the consumption for basic electro-chemical reaction as well as additional consumption due to current efficiency loss, secondary reactions with air, anode gases and other processes. In every smelter carbon plant, efforts are made to adjust anode manufacturing processes to sustain anode quality despite changing raw material quality. Pot operational parameters and practices are also optimised to minimise excess carbon consumption so as to reduce any negative impact on metal production cost. For example, the quality of calcined petroleum coke is variable, and sulphur content and metallic impurities are increasing. Use of different quality cokes impacts anode quality, which in turn affects anode performance and consumption in reduction cells.

Several papers have been published on the influence of anode properties and pot operation parameters on NCC [1, 2]. Other papers analyse specific anode properties as well as the influence of coke properties and of coke calcination on anode properties [3 – 12].

In this paper, analysis of three-and-a-half years’ data from EMAL (EGA Al Taweelah) is presented. The analysis shows how anode properties are influenced by anode manufacturing processes; and the ultimate impact on NCC.

2. Anode Consumption

Overall anode consumption is the sum of the following:

- Electrochemical formation of carbon dioxide,

- Electrochemical formation of carbon monoxide,
- Carboxy (Boudouard) reaction,
- Air burn, and
- Dusting as a consequence of preferential oxidation.

Theoretical carbon consumption is a result of the electrolytic reduction of alumina to aluminium according to Equation (1), which is for 100 % current efficiency.

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

Electrolytic carbon consumption takes into account current efficiency loss due to reoxidation reaction, Equation (2).

$$2Al + 3CO_2 = Al_2O_3 + 3CO \tag{2}$$

In this process, the mass of generated carbon monoxide is 7.1 % of mass of CO_2.

Excess carbon consumption is due to carboxy reaction, anode air burn and dusting. Carboxy or Boudouard reaction is the reaction of primary CO_2 gas with the anode carbon according to Equation (3):

$$CO_2 + C = 2CO \tag{3}$$

This reaction is favourable above 930 °C. There is a gas bubble layer underneath the carbon anode bottom surface. The gas bubble layer prevents CO_2 reacting with the anode carbon. However, because of hydrostatic pressure of about 3 to 4 kPa, CO_2 diffuses through the anode and then reacts at the chemically active surface, thereby generating CO.

Air burn relates to the attack on exposed carbon surfaces above the electrolyte level by atmospheric oxygen as per Equation (4). This results in significant loss of carbon during the anode life, especially during the initial period after anode setting in the pot. The impact depends on pot design, anode setting pattern and method of anode covering or protection with crushed bath-alumina mix.

$$C + O_2 = CO_2 \tag{4}$$

Dusting refers to the loss of carbon due to selective oxidation of binder coke. Selective oxidation occurs either due to less than required pitch, under-baking of anodes or a combination of both factors.

Figure 1 and Figures 2 to 4 [2] illustrate the anode consumption in the pots. Table 1 quantifies the carbon consumption during the production of primary aluminium.

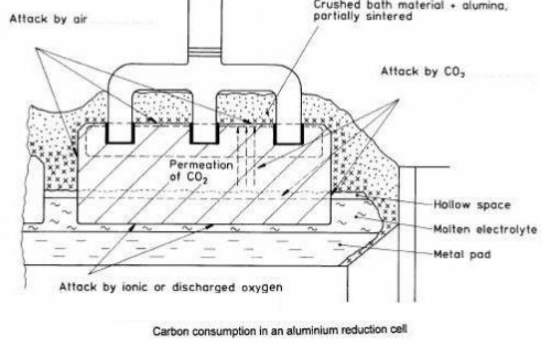


Figure 1. Reactions in the pot.

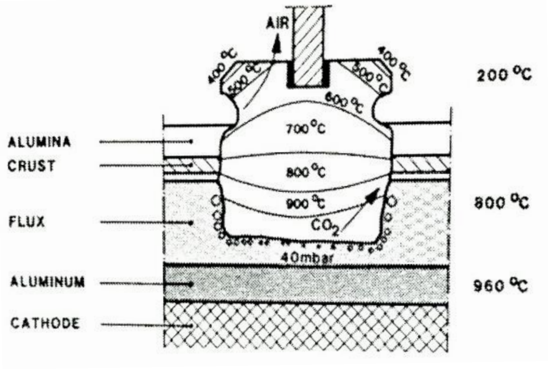


Figure 2. Anode consumption in the pot.

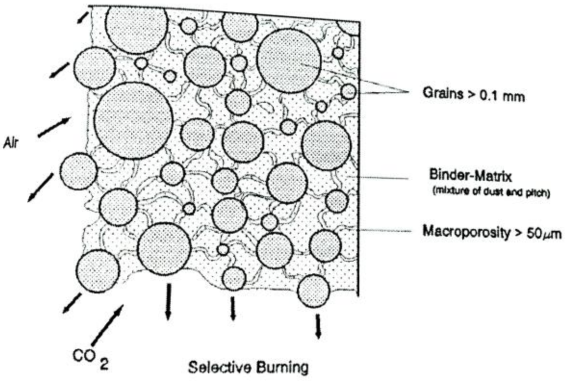


Figure 3. Selective oxidation of pitch coke.

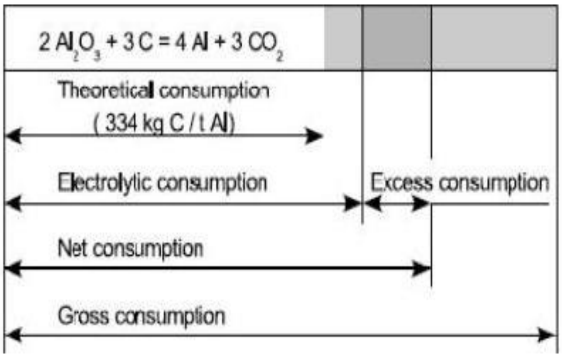


Figure 4. Carbon consumption.

Table 1. Carbon anode consumption.

Mechanism	Anode consumption, mass % prebaked cells
Basic reaction: $2Al_2O_3 + 3C = 4Al + 3CO_2$	66 to 76
Excess consumption: $C + O_2 = CO_2$ and $2C + O_2 = 2CO$	8 to 15
CO_2 burning: $CO_2 + C = 2CO$	5 to 6
Unreacted dust	0.3
Re-oxidation of metal	7 to 8
Pyrolysis and vaporisation	0.2
Sulphur, metal impurities and carbon loss by butts return	3.5 to 4.5
Net carbon consumption [kg C/t Al]	400 to 450

3. Plant Parameters

The EMAL smelter, located at Al Taweelah in Abu Dhabi, United Arab Emirates, has an installed capacity of 1.35 million tonnes of aluminium per year. The smelter has 1 200 electrolytic cells, of which 756 DX Technology cells operate at 388 kA and 444 DX+ Technology cells operate at 455 kA. The electrolytic cells use prebake carbon anodes, manufactured in two captive carbon plants. The paste plants, baking kilns and rodding plants operate the latest state-of-the-art technologies for green anode manufacturing, baking green anodes, rodding baked anodes and processing butts. The characteristics of the cokes used and the process parameters of manufacturing green and baked anodes are given in Table 2 and Table 3.

This paper presents correlations noted between anode manufacturing parameters and baked anode properties, and their impact on the net carbon consumption in electrolytic pots. Anode reactivities affect the carbon consumption in the pots during the electrolysis of alumina. Pitch content in anodes, impurities in anodes and anode desulphurization during baking were studied to find their influence on anode reactivities.

The study is based on data from the EMAL smelter over a three-and-half year period of operations (January 2012 to July 2015). Process data from the paste plant and baking kiln was used, along with the laboratory analysis of raw materials and baked anode core samples.

Table 2. Typical characteristics of calcined petroleum cokes (CPCs) used at EMAL smelter.

Analysis	Unit	Coke A	Coke B	Coke C
		average	average	Average
Fe	%	0.014	0.007	0.002
Si	%	0.014	0.001	0.003
S	%	2.57	1.05	2.83
V	%	0.024	0.005	0.019
Ni	%	0.022	0.008	0.009
Ca	%	0.013	0.001	0.001
Na	%	0.006	0.004	0.002
Ash	%	0.19	0.05	0.08
Moisture	%	0.06	0.08	0.08
Real density	g/cm³	2.081	2.072	2.079
Vibrated bulk density (VBD).	g/cm³	0.938	0.925	0.864
Volatile matter (VM)	%	0.40	0.44	0.42
Hard grove index (HGI)	no	31.5	36.0	31.8
+ 4 Mesh	%	36.3	27.4	35.3
- 20 Mesh	%	24.6	26.1	22.9
CO2 reactivity	%	12.2	7.0	2.7
Air reactivity	%/min	0.29	0.07	0.07
Electrical resistivity	µΩ.m	464.4	441.5	492.8
Lc	nm	3.09	2.88	3.05
Calciner type		Shaft	Rotary	Rotary

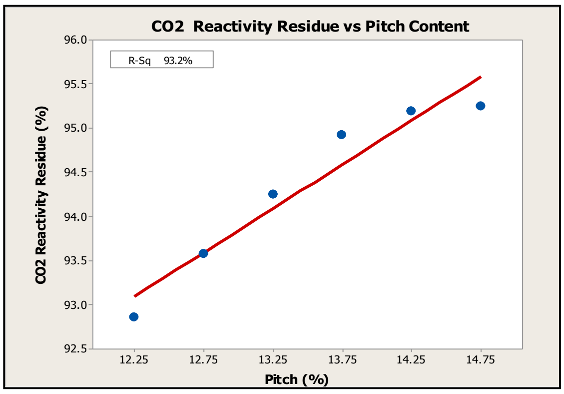
Table 3. Anode manufacturing parameters at EMAL smelter.

Parameter	Unit	Value
Dry aggregate GSR	No.	3.5 to 4.5
Pitch content	%	12.5 to 14.5
Mixer energy	kWh /t paste	7.5
Vibro-compaction time	s	45 to 55
Top tool pressure	kPa	250 – 450
Vacuum	kPa	2 to 3
Baking temperature	°C	1160 to 1190

4. Findings

4.1. Pitch addition

The study shows that, with increases in pitch addition, the baked anode CO_2 reactivity residue (CRR) increased (Figure 5) while CO_2 reactivity dust (CRD) reduced (Figure 6).



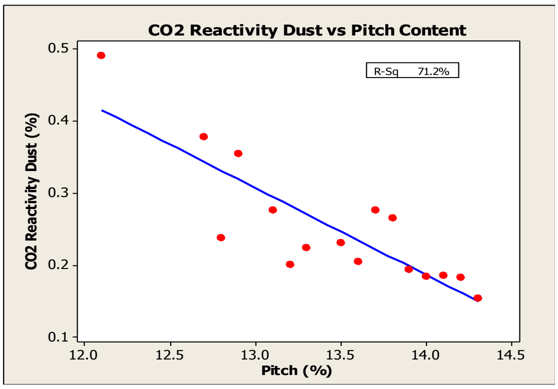
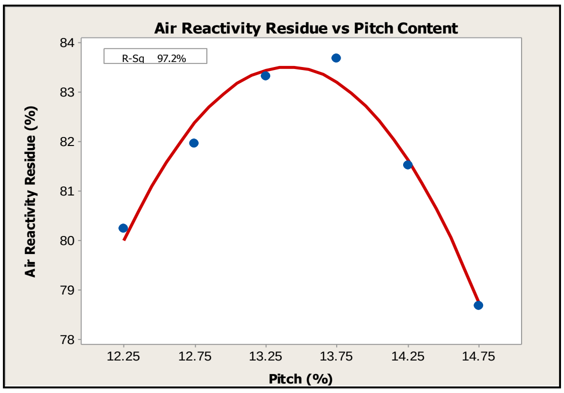


Figure 5. CO_2 reactivity residue vs. pitch.

Figure 6. CO_2 reactivity dust vs. pitch.

The baked anode air reactivity residue increased (Figure 7) while air reactivity dust reduced (Figure 8) with increased pitch addition. The permeability of baked anodes first decreased to a certain level of pitch addition and thereafter increased exponentially (Figure 9).



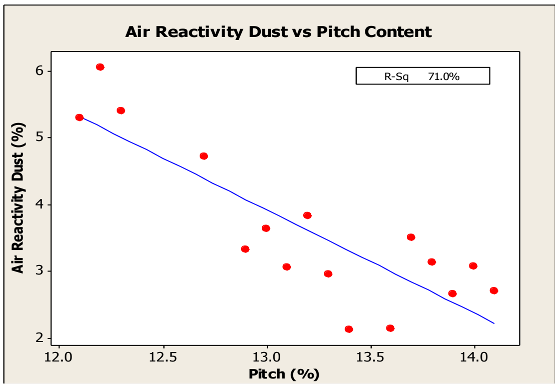


Figure 7. Air RR vs. pitch content.

Figure 8. Air RD vs. pitch content.

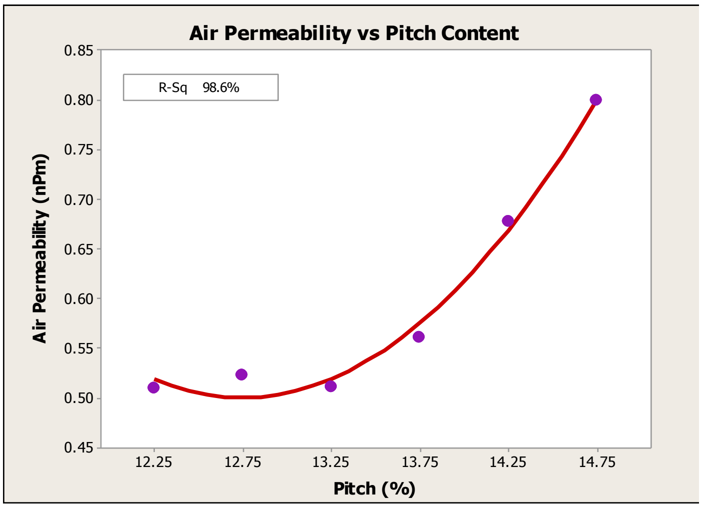


Figure 9. Air permeability vs. pitch content

4.2 Impurities

Impurities such as iron, calcium and sodium have an adverse impact on CO_2 reactivity residue. The impact is severe after 600 ppm limit (Figure 10). The air reactivity is adversely affected by the vanadium content of the anode (Figure 11).

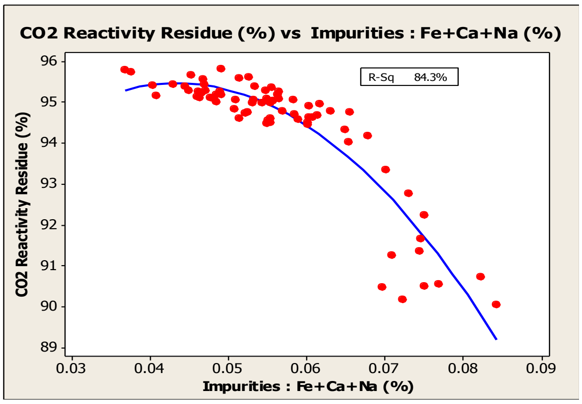


Figure 10. CO_2 RR vs. impurities.

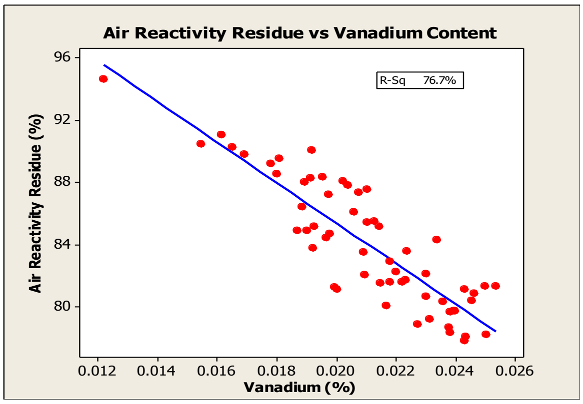


Figure 11. Air RR vs. vanadium.

4.3 Desulphurization of anodes

During the baking process, there is desulphurizaion of anodes. Peak flue temperature is found to affect desulphurization (Figure 12). It is also impacted by the sulphur content in the coke used for anode manufacturing (Figure 13).

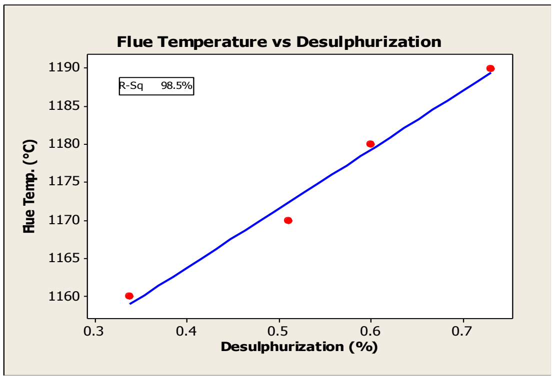


Figure 12. Flue temp. vs. desulphurization.

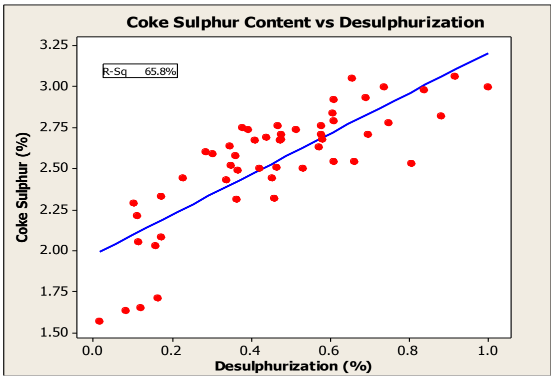


Figure 13. Coke S vs. desulphurization.

It was observed that the anode desulphurization reduces CO_2 reactivity residue (Figure 14). Anode air permeability increased with increase in desulphurization during the baking process (Figure 15).

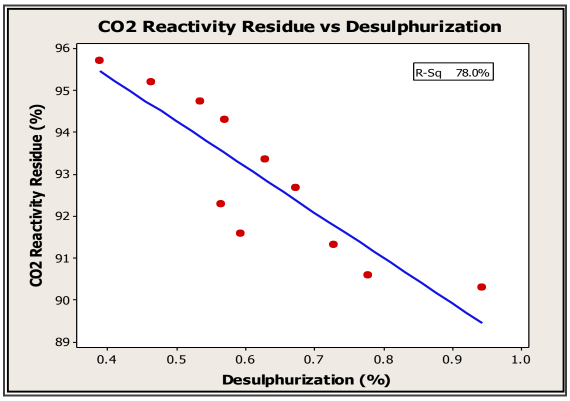


Figure 14. CO2 RR vs. desulphurization.

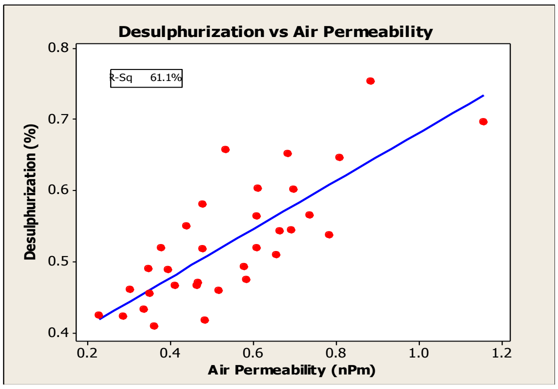


Figure 15. Desulphurization vs. permeability.

5. Discussion

CO_2 reactivity residue is the result of reactivities of the base coke and filler pitch coke phases. At adequate baking levels, pitch coke reactivity becomes a controlling factor. With increasing pitch addition, there is more pitch coke that has lower metallic impurity content and therefore is less reactive. Due to better filling of coke pores by the binder (mix of pitch and ultra-fines), there is a gradual decrease in air permeability and the reactive surface area of anodes. Lower reactive surface area and lower metallic impurities reduce anode reactivity and help reduce carbon consumption in the pots. Higher CO_2 reactivity residue at higher pitch levels could be explained due to better bridging effects between coke particles by the higher quantity of pure pitch coke. Not only the anode reactivity is reduced, but also CO_2 reactivity dust is reduced. This prevents carbon dusting in the pots. Figure 16 shows the relationship between CO_2 reactivity residue and net carbon consumption.

Metallic impurities such as sodium, calcium, iron and vanadium are found to have a catalytic effect on the reaction between carbon and oxygen above 450 °C and an adverse impact on air reactivity. The temperature of the exposed surface of the anode (i.e. above the electrolyte) increases over the anode's life in the pot; the carbon begins to react with oxygen, the reaction rate increasing with greater temperature and higher impurity levels. It is thought that metallic impurities in anodes act as catalysts and encourage the burning of carbon. A decrease in air reactivity residue, which indicates increase in reactivity towards air, increases net carbon consumption (Figure 17).

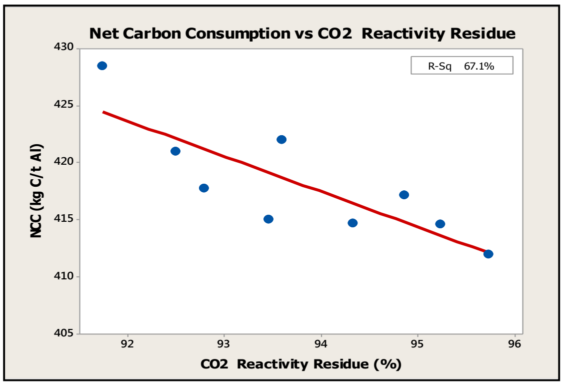


Figure 16: NCC vs. CO2 RR.

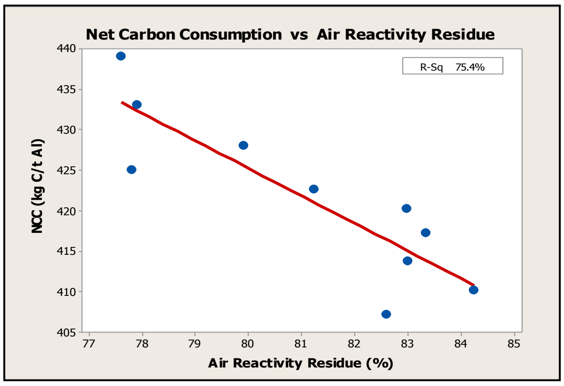


Figure 17: NCC vs. air RR.

The pitch coke bridges holding coarse particles together are consumed preferentially if the anodes have not been baked to the optimum level, or if the pitch addition to the anode is insufficient. The coarser particles detach themselves and fall into the bath. This impacts the electrolyte resistance and pot temperature, leading to a drop in current efficiency and an increase in carbon consumption. It is necessary to bake anodes sufficiently such that the real density of anode is equal to or higher than the real density of the calcined petroleum coke (CPC). This ensures that the reactivity of the pitch coke is equal to the reactivity of the base coke, so that preferential oxidation of the pitch coke does not occur in the pots.

During the baking of green anodes, some sulphur is released from the anodes. This process, known as desulphurization of anodes, is dependent on the peak flue gas temperature and the soaking time of the baking cycle. The sulphur is released mainly from the calcined petroleum coke. Coke is produced nowadays by processing more sour crudes, which have higher sulphur content and higher content of metallic impurities. During the calcination of green coke, there is some coke desulphurization as well as destabilization of the bonds between carbon and sulphur atoms. The degree of coke desulphurization and destabilization of carbon to sulphur bonds depends on the calcination temperature and the residence time of the coke inside the calciner kiln. The sensitive, destabilized bonds between carbon and sulphur in calcined petroleum coke are prone to break during the anode baking process, thus leading to further desulphurization of the anodes. The higher the sulphur content in the coke, the higher the degree of desulphurization. The increase in the chemically reactive surface area of the anodes, coupled with the absence of inhibiting sulphur atoms (due to anode desulphurization), decreases the CO_2 reactivity of the anodes. Anode desulphurization increases the permeability of anodes. These changes in the anode properties, and the hydrostatic pressure of the gas layer at the anode bottom surface in the pots, encourage percolation of CO_2 into anodes to react with carbon to produce carbon monoxide. The Boudouard reaction is favoured at pot operating temperatures of 960 °C. The sulphur itself could act as an inhibitor to this secondary reaction; however, due to desulphurization, the secondary reaction is favoured.

The net carbon consumption is found to increase with increasing desulphurization (Figure 18).

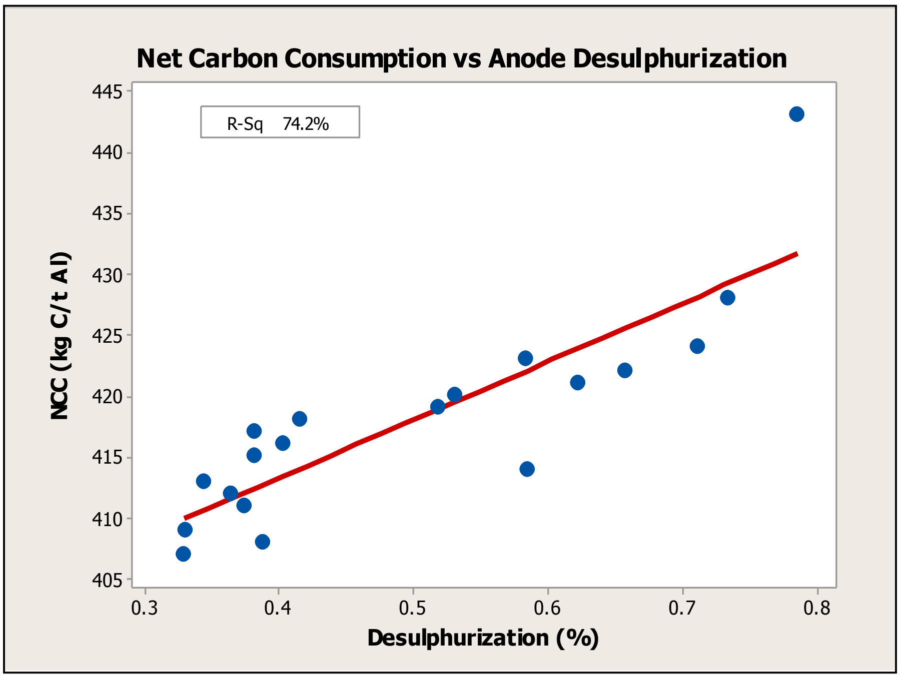


Figure 18: NCC vs. anode desulphurization.

The baking level of anodes, which depends on maximum flue temperature and the soaking time of the baking cycle, should be optimised such that anode desulphurization is as low as possible. However, care needs to be taken to ensure that the pitch coke reactivity is almost equal to the reactivity of the main coke.

The use of high real density cokes necessitates the baking of anodes at high temperatures. Because of the high baking temperatures and high sulphur content in cokes, there is anode desulphurization which in turn results in degradation of the anode performance in the pots. Anode desulphurization can be avoided by baking anodes at temperatures where anode desulphurization is about to begin. The resultant pitch coke reactivity will be low, but high enough to be equal to that of low real density cokes. Therefore, to prevent preferential oxidation of the pitch coke and to increase the pitch coke reactivity equal to the main coke reactivity, use of low real density cokes as the base cokes could be an option. Green coke calcined at lower temperatures yields low real density calcined cokes with reduced desulphurization and low instability of carbon to sulphur bonds. Anodes made with low real density calcined cokes are likely to desulphurize to a lesser extent during baking. Anodes that have not been desulphurized, and with reactivities of both coke phases being nearly the same, would have reduced secondary carbon consumption in the pots, therefore lower net carbon consumption.

6. Conclusions

- Anodes with higher pitch content have higher CO_2 reactivity residue and lower CO_2 reactivity dust, both of which are favourable in reducing net carbon consumption.
- Anodes with higher metallic impurity content have lower CO_2 reactivity residue and higher CO_2 reactivity dust, which increase net carbon consumption.
- Higher baking temperatures favour desulphurization of anodes. Desulphurization of anodes lowers CO_2 reactivity residue while increasing air permeability, thereby resulting in increased net carbon consumption.
- Pitch addition, impurity content and desulphurization need to be optimised by adjusting anode manufacturing parameters to reduce net carbon consumption.

It appears logical to use low real density coke to make anodes, because these anodes could be baked at temperatures such that there is no desulphurization, yet the reactivities of base coke and pitch coke are almost equal. This could result in lowering the net carbon consumption.

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