

CB13 - Impact of Sulphur Content on the Electrical Resistivity of Carbon Anodes

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Abstract

Prebaked carbon anodes are used in the production of aluminium by the Hall-Heroult electrolysis process. Carbon anodes that are produced in captive carbon plants, using calcined petroleum coke, coal tar pitch, and butts as the main raw materials, have a critical role in the operation of electrolysis cells. The carbon anodes contribute towards cell voltage drop. The voltage drop of carbon anodes influences energy consumption per tonne of aluminium metal production. The anode electrical resistivity ranges from about 50 $\mu\Omega$ m to as high as 65 $\mu\Omega$ m. The industrial data of carbon anode properties, raw materials, and manufacturing processes were analyzed. The correlations of anode electrical resistivity with raw material characteristics and process parameters are presented in the paper. The paper explains why sulphur affects the electrical resistivity of carbon anodes. Actions to achieve low anode electrical resistivity have been proposed to reduce the electrical energy consumption of the electrolysis process, thereby improving financial savings, and reducing carbon footprint.

Keywords: Carbon anode, Calcined petroleum coke. Dry aggregate, Baking temperature, Electrical resistivity.

1. Introduction

Modern aluminium smelter plants operate at 300 to 500 kA current and use prebaked carbon anodes to produce aluminium. Prebake carbon anodes are manufactured in captive carbon plants with the latest state-of-the-art technologies for green anode manufacturing, baking green anodes, sealing baked anodes with stem brackets, and units to process the bath and butts.

Requirements of carbon anode properties are very stringent due to severe operating conditions in high kA cells. Optimum quality carbon anodes are needed for the smooth operation of electrolysis cells. The carbon anode properties are influenced by the properties of raw materials used, and the process and equipment parameters at every stage of anode manufacturing.

This paper deals with anode electrical resistivity. The anodes are required to have low electrical resistivity. Electrical resistivity has implications on voltage drop through carbon anodes. Higher resistivity increases the voltage drop of electrolysis cells, leading to increased power consumption, thereby cost of metal production. Figure 1 shows the increase in power consumption due to anode electrical resistivity increase, for an aluminium smelter having 360 pots operating at 365 kA current. It also has implications for the greenhouse effect due to increased power consumption. The paper analyses industrial data and presents correlations between baked anode electrical resistivity, raw material properties, and process parameters at every stage of anode manufacturing.

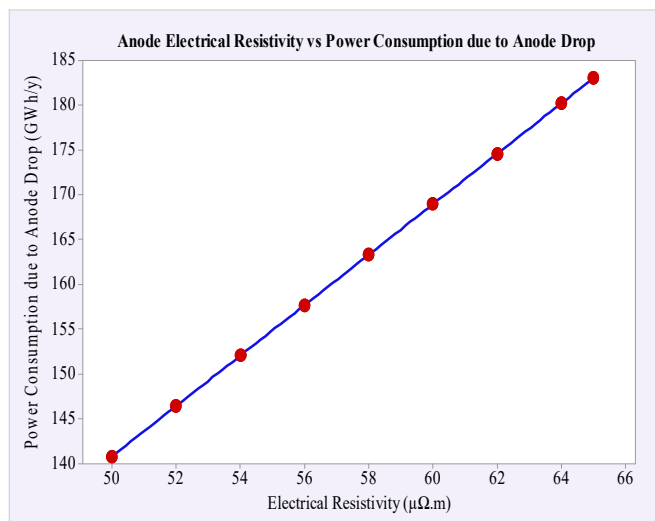


Figure 1. Anode electrical resistivity vs, power consumption due to anode voltage drop.

2. Findings

Analysis of baked anode properties indicates a relationship between sulphur content and electrical resistivity.

The sulphur content of baked anodes depends on:

- a) Sulphur content of the cokes and butts in the dry aggregate of anodes.
- b) Pitch content in the anodes
- c) Baking level of anodes, due to thermal desulphurization.

2.1 Sulphur Content of Calcined Petroleum Cokes

Carbon plants use calcined petroleum coke as the main component of the dry aggregate of anodes. Calcined petroleum cokes are obtained by calcining green cokes in either rotary kilns or vertical shaft kilns. Green cokes are byproducts of crude oil refineries. Oil refineries use sweet as well as sour crudes. Sweet crudes have low sulphur content while sour crudes have high sulphur content. The sulphur content in cokes depends on the source and type of crude oils and on the final temperature of the calcination of green cokes.

The sulphur content in the calcined petroleum cokes available now is in the range of 2.5 - 3.5 %. However, a few calcined petroleum cokes have a sulphur content of about 1 - 2 %. Low sulphur cokes are limited due to the depletion of sweet crudes. The major tonnage of cokes available today has high sulphur content.

Aluminium smelters have not changed the specifications for sulphur content in cokes on account of environmental emission limits; therefore, the anodes are produced using blends of high-sulphur cokes and low-sulphur cokes. Because of the blending of cokes in varying proportions, the sulphur content of the coke mix entering the paste plant varies according to the source of coke, the blend ratio, and the type of coke calcination.

2.2 Pitch Content in the Anodes

Pitch demand by the dry aggregate during the green anode manufacturing stage is influenced by the vibrated bulk density of the cokes. The addition of less quantity of pitch may result in a lesser physical contact at the interface between coke particles and pitch, than when optimum or more

than optimum quantity of pitch is added. It is also to be noted that sulphur content in coal tar pitch is low, about 0.5 - 0.8 %. As we increase the pitch content in green paste, the average sulphur content of the green paste decreases, thereby leading to an overall reduction in the sulphur content of anodes.

2.3 Baking Level of Anodes

Because of destabilized carbon-sulphur bonds created during coke calcination, some of the sulphur atoms leave the anode during anode baking, and this leads to the desulphurization of anodes (Figure 2). The removal of Sulphur is recommended during calcination as first stage, and anode baking as a second stage. The higher the temperature of anode baking, the higher the desulphurization of anodes.

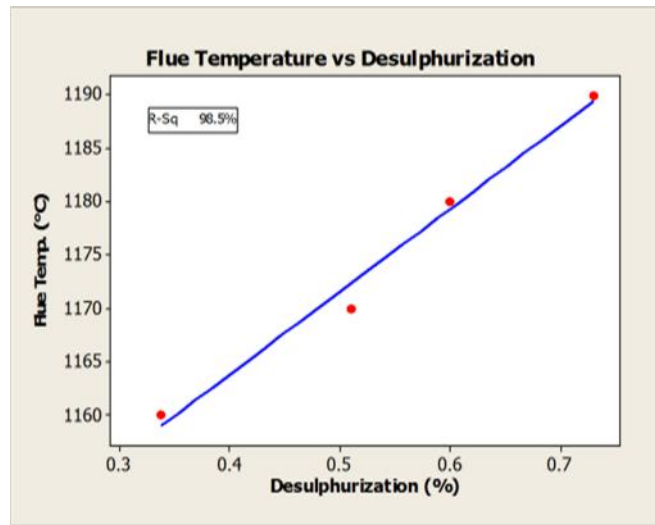


Figure 2. Desulphurization of anodes during baking.

It is also found that the anodes with higher sulphur content undergo higher desulphurization (Figure 3). Anodes were baked at a temperature of 1180 °C.

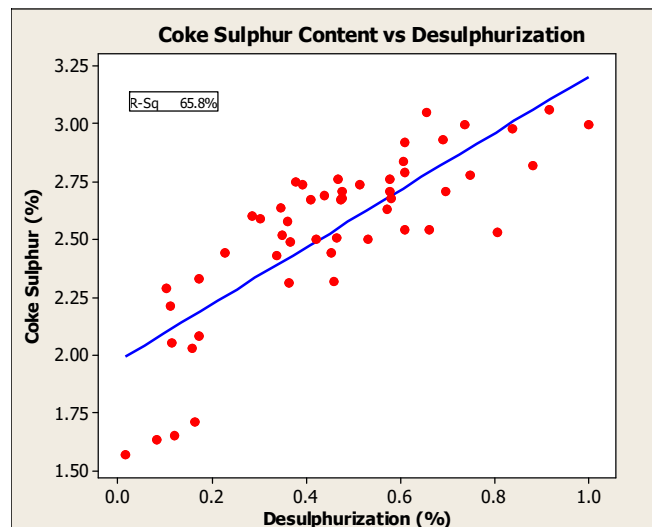


Figure 3. Sulphur content in cokes vs. desulphurization.

2.4 Electrical Resistivity of Anodes

Industrial baked anode properties show a good relationship between sulphur content and electrical resistivity. Baked anode electrical resistivity increases with increasing sulphur content (Figure 4 and Figure 5). The data is from the baked anode properties of EMAL and Aditya Aluminium.

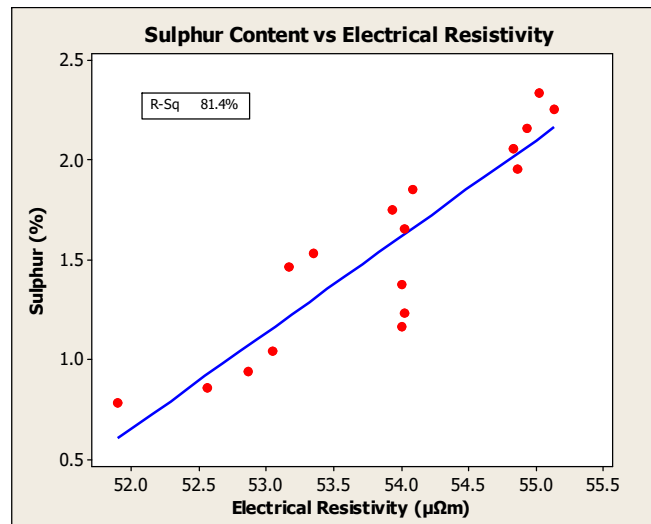


Figure 4. Sulphur content in baked anodes vs. anode electrical resistivity.

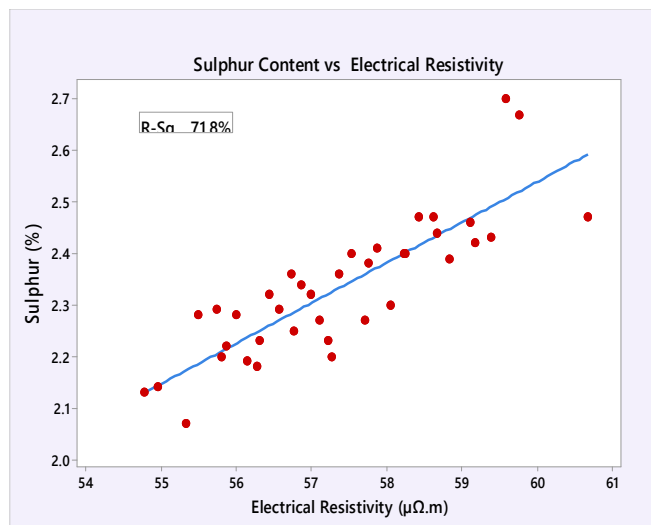


Figure 5. Sulphur content in baked anodes vs. anode electrical resistivity.

3. Discussions

The sulphur content of baked anodes is influenced by the coke calcination, pitch addition to the paste and anode baking.

3.1 Coke Calcination

During calcination, there is desulphurization of cokes [1,4]. Desulphurization of cokes increases with increasing calcination temperature (Figure 6). The desulphurization of cokes with high sulphur content is higher compared to that of low sulphur cokes. Higher calcination temperatures result in a higher decrease in coke electrical resistivity [2]. During desulphurization, some sulphur

atoms remain with coke because the energy required to drive them out was not sufficient. These sulphur atoms will leave the carbon anodes during baking [3].

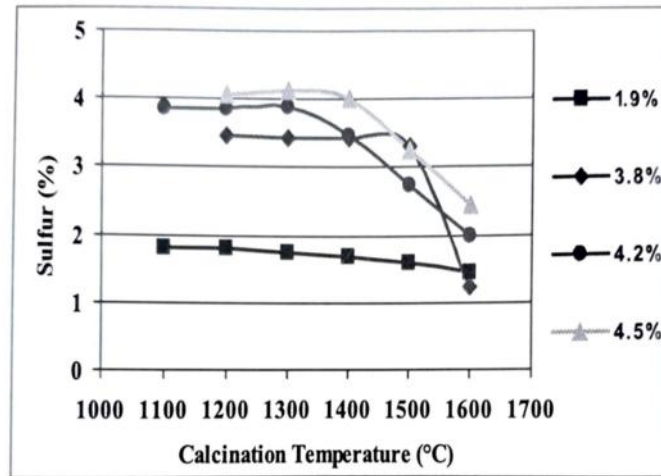


Figure 6. Coke calcination temperature vs. sulphur loss [3].

It is also observed that desulphurization is higher in high-sulphur green cokes (Figure 7).

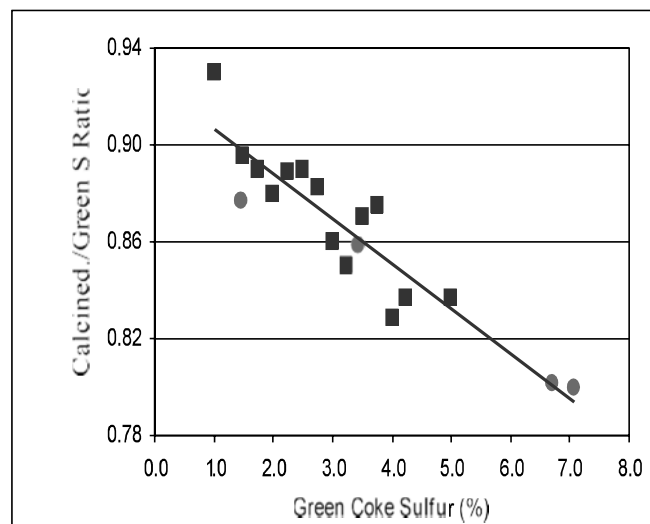


Figure 7. Desulphurization of green cokes during calcination [3].

3.2 Pitch Addition

Coal tar pitch has relatively low sulphur content, in the range of (0.5 – 0.8) %. It is converted to pitch coke during anode baking. The pitch coke is pure, with lower sulphur content and elemental impurities. With the increase in pitch addition, the quantity of coke with low sulphur content increases in anodes. There is an overall reduction in the sulphur content of anodes. Increased pitch addition increases contact between coke grains due to near complete coating of them. Reduction in sulphur content and increase in contact at the particle interfaces are likely to explain the reducing trend of anode electrical resistivity. The graph in Figure 8 shows the changes in anode electrical resistivity with the addition of an optimum or more than the optimum quantity of pitch to the anode.

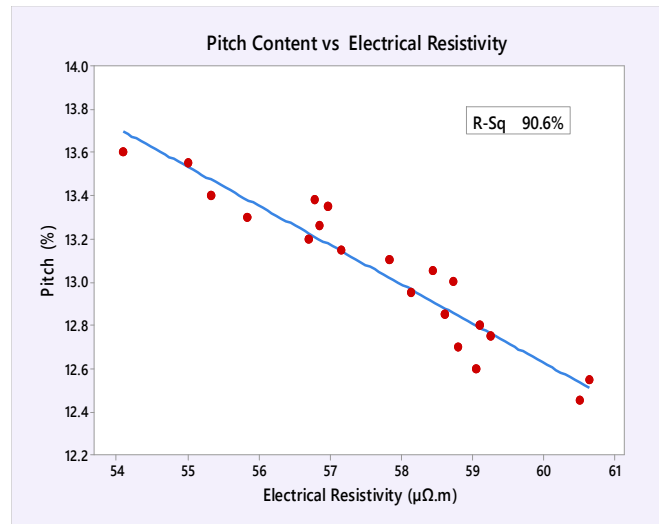


Figure 8. Pitch content in anodes vs. electrical resistivity

3.3 Anode Baking

During the baking of anodes, the sulfur atoms destabilized during coke calcination get released, resulting in loss of sulphur from anode mass. The loss of sulphur increases with an increase in peak baking temperature and soaking time (Figure 9). It is accompanied by a decrease in anode electrical resistivity [2, 3]. Desulphurization, if it is at higher extent, can increase porosity of anodes. It provides more surface area for reactants leading to slight increase in net carbon consumption. For reducing Boudard reaction at 960 °C, certain amount of sulphur is desirable. As we are having already higher content of sulphur in anodes this becomes irrelevant as there is already sufficient sulphur in anodes to control Boudard reaction.

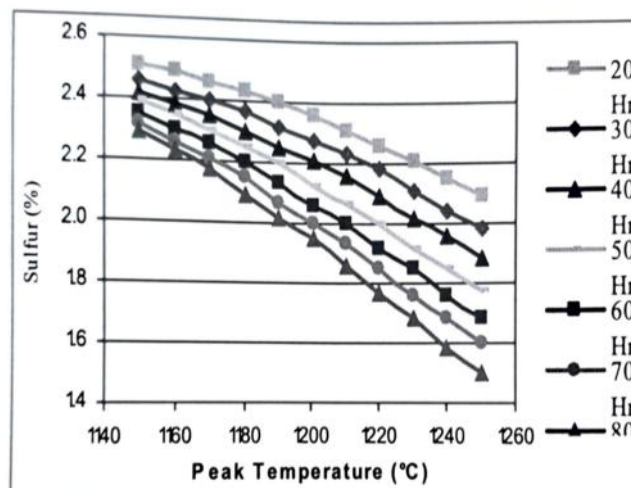


Figure 9. Anode baking temperature and soaking time vs. decrease in sulphur content [3].

3.4 Anode Electrical Resistivity

Anodes having higher sulphur content show higher electrical resistivity.

Electrical resistivity is influenced by the availability of electrons that flow through the anode mass. Each carbon atom has two electrons in its outer orbit, and these electrons are released easily from the outer orbit to achieve orbital stability. The electrons from the outer orbits of carbon

atoms are available as “free electrons”. The free electrons ensure the flow of electricity through the anode mass. As opposed to this, each sulphur atom has six electrons in the outer orbit and needs two electrons to fill its outer orbit to achieve orbital stability. These electrons are made available from carbon atoms. The higher the number of sulphur atoms in carbon anode mass, the higher the number of free electrons captured by sulphur atoms, reducing the number of free electrons available for conducting electricity. It may therefore be said that the anode electrical resistivity is influenced by and increases with an increase in sulphur content. Sulphur content in anodes is influenced by the sulphur content in calcined petroleum cokes, the quantity of pitch added to the anodes, and the level of anode baking.

Coke calcination, anode baking and pitch addition may be considered as routes to reduce sulphur content in coke and anode, and the electrical resistivity of carbon anodes.

4. Conclusions

Sulphur content in carbon anodes depends on the cokes used, pitch addition to the anode and baking level of anodes.

There is a good relationship between sulphur content in anodes and anode electrical resistivity.

Anode electrical resistivity increases with increasing sulphur content in anodes.

Anode electrical resistivity can be kept at a lower level by controlling sulphur content in anodes by blending high-sulphur cokes with low-sulphur cokes, by keeping pitch addition in anodes at a higher than optimum level and by baking anodes at higher temperatures.

5. References

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