# CB04 - Impact of Quality Changes in Calcined Petroleum Coke (CPC) on Anodes Used for Aluminium Production

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**Abstract**



Calcined Petroleum Coke (CPC) has been in use for more than 120 years to produce the carbon anodes used in the Hall-Heroult Aluminium electrolysis process. Performance of the anodes in the aluminium electrolysis process depends on many properties of CPC. It is seen that over the last several years quality and availability of anode grade petroleum coke has been impacted by changes in the petroleum refining industry. Refineries have started using sour crudes that have high sulphur and metallic impurities due to shortage of sweet crudes coupled with high demand for oil. As a result, RPC from refineries are having higher sulphur content and metal impurities. Therefore, smelters worldwide are using CPC with higher sulphur content to meet their requirements. The increasing trend of impurities in CPC used by Indian industry is a major concern for the industry. In this paper, the quality variations observed in CPC used by NALCO and their impact on anode quality is highlighted along with presentation of few R&D studies carried out at NALCO, the findings of which may be helpful to deal with expected future quality changes in CPC.

**Keywords:** Calcined Petroleum Coke, Anode, impurities.

## 1. Introduction

Calcined petroleum coke (CPC) is one of the major raw materials for the Aluminium Industry. Like any other raw material, it plays a significant role in the aluminium production process. CPC is used for fabrication of anodes used in the aluminium electrolysis process. Extensive research is taking place since more than 30 years to find an alternative to this material. From the recent reports [7][8], it is evident that though considerable progress has been made in finding right kind of materials for making inert anodes, it may take many years to address the impending problems associated with fabrication and use of inert anodes. Hence today more focus is required on the carbon anodes made out of CPC & coal tar pitch (CTP) for continual improvement of performance of the electrolytic pots producing aluminium metal.

In the present day, the global production of primary aluminium is around 64 Mt, China being the single largest producer of aluminium contributing to 57 % of total world production. The global demand of aluminum has grown at an average rate of 4.5 % in the past five years. If the same trend continues in future, by 2025 the aluminum production will reach a level of about 87 Mt/a. Primary aluminium installed capacity in India is today 4.1 Mt with expansion plans and other development plans in place. Further, the Indian aluminum demand has grown at an average rate of 12 % in the past four years. If the same trend continues in future, by 2025 the Indian aluminum production will reach a level of about 8 Mt/a, which means increasing the production capacities. In accordance to increase of aluminium capacity, requirement of CPC for Indian aluminium industry is going to increase from the current 1.3 Mt to 2.6 Mt. Availability of suitable grade of CPC for anode production is going to be a challenge for the Indian Aluminium industry. There is a shortfall of 92 % CPC with <1.25 % S and 82 % CPC with 2.5 % S in India. It is seen that over the last several years quality and availability of anode grade petroleum coke has been impacted by changes in the petroleum refining industry. The refineries have started using sour crudes that have high sulphur and metallic impurities due to shortage of sweet crudes coupled with high demand for oil.

National Aluminium Company (NALCO) established in 1981 in the state of Odisha has its smelter complex situated at Angul. The plant has been set up in technical collaboration with aluminium Pechiney and operates the AP18 pots in four potlines having total 960 pots augmented with its own carbon plants equipped with most advanced technology producing prebaked anodes NALCO, since its inception has been using CPC of different varieties. This paper focuses on the impact of various properties of CPC on the anode quality. A few R&D studies carried out to find possible solutions to improve anode quality in the face of deteriorating CPC quality are included in this paper.

## 2. Calcined Petroleum Coke

### 2.1 Crude Oil to Coke

The choice of crude processed in a refinery is strongly affected by location of crude and refinery design and is normally independent of coke quality considerations. Crude oil has an elementary composition C: (84-87) %, $H_2$: (11-14) %, S: 0.2 %, $N_2$: 0.2 % and is a mixture of hydrocarbons which range in boiling points from 0-80 °C. It is distilled under atmospheric pressure followed by a distillation under vacuum. Typical products from a barrel of crude oil are light straight run gasoline 11 %, reformer naphtha 25 %, kerosene 15 %, diesel fuel 10 %, gas oil 10 % and residue-coker feedstock 8 %. The residue is heated to approx. 500 °C and is directed to the bottom of one of the coke drums. Here sufficient retention time (32 h) and temp is provided in order to permit a slow formation of coke (hence the term delay coking).

### 2.2 Coker Products

1. Shot coke; it is spherical in shape 2- few (25 cm) in size, have high CTE; have a slick shining exterior coating of needle type carbon.

2. Fuel coke; fuel coke has a less optimal macrostructure, has a high coefficient of thermal expansion (CTE). It is the least valuable material in the non-fuel market.

3. Sponge coke; sponge coke or honeycomb coke, the pore structure is more pronounced and CTE is decreased. This is the anode grade coke.

4. Needle coke; it has a characteristic needle like surface. This coke has the lowest CTE and low in metals and sulfur. Most of the graphite manufacturers use this coke.

### 2.3 Raw Petroleum Coke (RPC) to Calcined Petroleum Coke (CPC)

Raw petroleum coke is calcined to remove excess water and volatile matter in rotary kilns or shaft kilns. Rotary kilns are most widely used for economic reasons. Calcination temps are between (1250-1400) °C. The calcined coke leaving the kiln is discharged into a rotary cooler, where it is quenched with direct water spray at the inlet and then cooled by a stream of ambient air. The calcining operation can have an important influence on coke quality. Cokes with significantly different volatile contents (quality and quantity) and impurity levels should be calcined differently. Calciner process variables affecting CPC quality is given in Table 1.

From the above experiment it could be observed that by using boric acid doped CPC for making anodes, the $CO_2$ and Air reactivity residue of anodes improve significantly. This solution can be adapted by coke calciners in consultation with aluminium smelters. A measured quantity of boric acid can be added at calciner by making special arrangements, to produce low reactive CPC. Boron limit can be given in the specification of CPC by the smelters.

## 8. Dealing with High Sulphur Cokes

Sulphur levels may continue to rise due to practises of blending of fuel grade coke with anode grade cokes at the coking/calciner's operations for lowering the cost. In order to meet environmental norms, $SO_2$ scrubbing may be adopted more widely in the future by calciners and smelters. Desulphurisation during anode baking needs to be checked by maintaining baking homogeneity in anodes and avoiding excessive high anode baking temperatures.
At present sulphur level of CPC used by NALCO remains below 3 %. It is observed that when % S in few CPC supplies is > 2.5 %, the $CO_2$ reactivity of anodes made from such cokes is significantly higher than the $CO_2$ reactivity of anodes made from CPC with S < 1.5 %.

## 9. Summary and Conclusions

In this paper, the aluminium industry's experience in dealing with the impact of utilising calcined petroleum coke with lower density and higher impurities on anode quality in the recent years has been described. It has been shown [5] that blending of cokes at calciners and smelters will remain the dominant strategy to deal with the issue of quality changes. Impact of blending of CPC of different qualities, impact of blending only the fines fraction of CPC having lower impurities, impact of process parameters i.e. paste mixing temperature and Blaine number on anode quality have been presented in the paper.

Increase in Sulphur, Vanadium & Nickel in CPC will remain the most obvious quality changes in future. To deal with the issues of reactivity of anodes i.e. higher air reactivity losses due to high vanadium CPC it is suggested to add boric acid in controlled manner without affecting the metal purity. This methodology has been adapted by NALCO. The results of plant data are shown in this paper. It has also been experimented that if CPC is pre-treated with boric acid at any suitable point in the calcining process, the anodes made out of such cokes have superior Air & $CO_2$ reactivity values.

The R&D studies presented in this paper may become useful for Aluminium Industries to address the problem of density and reactivity properties of anodes which may arise due to non-availability of suitable grade CPC at present and also in future. However, the role of calcining industry in supplying good quality CPC also remain significant.

## 10. References:

1. Werner K Fischer, *Anodes for Aluminium Industry (Compilation of papers)*, R&D Carbon Ltd., Switzerland.
2. Kirstine Louise Hulse, *Raw materials, formulation and processing parameters*, R&D Carbon Ltd., Switzerland.
3. Training manuals on Carbon Plant – AP18 Technology for National Aluminium Company Ltd.
4. Binuta Patra, A. Palchowdhury, Improvement in oxidation Behaviour of Prebake anodes used in NALCO smelter plant, *Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2-5 Oc. 2017, TRAVAUX 46, 731-742.*
5. Les Edwards, Evolution of Anode Grade Coke Quality, *Light Metals* 2012, 1208-1212.

6. https://www.lightmetalage.com/resources/patents/primary-aluminum-inert-anode-and-wettable-cathode-technology-in-aluminum-electrolysis/.
7. http://www.aluminum-production.com/inert_anode_technology.html.
8. Binuta Patra, *Process for preparing prebaked carbon anodes having improved oxidation resistance for aluminium production*, NALCO Patent, Filed 29/KOL/2011, dated 10.01.2011, Granted No 289807, dated 22.11.2017.
9. Binuta Patra, *Improvement in oxidation behaviour of calcined petroleum coke used for production of anodes in aluminium industry*, NALCO Patent, Filed 363/KOL/2014, Dated 21.03.2014.