Improvement in oxidation Behaviour of Prebake anodes used in NALCO smelter plant

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Abstract

In view of the importance of the anode carbon consumption on the economics of the Aluminium production process & CO_2 emission, great efforts have been made in recent years to study the problem. The excess carbon consumption due to air oxidation is mainly affected by the metallic impurities e.g. vanadium, nickel, sulphur present in the raw materials and calcium, sodium in recycled butts. Detailed studies have been carried out at NALCO Smelter Plant to understand the problem of excess anode carbon consumption during the electrolysis process .Experiments were carried out in laboratory scale, bench scale and plant scale by addition of boric acid in green anode recipe. The result of the one year plant level trial is presented in this paper. It could be established that there is significant improvement in air reactivity residue figures of anodes by addition of boric acid.

Keywords: Prebaked anodes, Air reactivity, boric acid.

1. Introduction

Aluminium is produced conventionally by the Hall Heroult process, by the electrolysis of alumina dissolved in cryolite containing molten electrolytes at temperatures around 955-960 deg C. In these Hall Heroult cells, the anodes are usually prebaked carbon blocks which are electrochemically consumed.

Prebaked anodes are made of a mixture of calcined petroleum coke and coal tar pitch. Production of these anodes involves various unit operations including preparing & treating the starting materials, metering, preheating, mixing, forming and baking at high temperature & then rodding for enabling the current supply to the pot.

The overall chemical reaction in the aluminium production is summarized as in equation (1)

$$2Al_2O_{3(dissolved)}+3C_{(solid)} \rightarrow 4Al_{(liquid)}+3CO_{2\,(gas)} \quad (1)$$

The theoretical consumption of carbon as per the reaction is 334 kg per one ton of aluminium produced. However the actual carbon consumption is 400-450 kg per ton of aluminium produced.

The extra carbon consumption is affected by the current efficiency of pots and various secondary reactions occurring during the process such as:

- Oxidising reaction with oxygen from air on the upper part of anodes if the anodes are not protected.
- Carbon oxidation reactions with CO_2 at the surface of the anode bottom immerse in liquid bath.
- Selective oxidation of binder pitch coke.

The carbon consumed accounts for 20-25% of Aluminium production cost.

Various additives have been tried to improve the oxidation resistance of anodes. The addition of phosphorous has been found beneficial in reducing the oxidation losses but phosphorus contamination in aluminium metal lowers the current efficiency. AlF_3 & Alumina have also been tried but have been found not very beneficial as far as overall improvement in oxidation behaviour of anodes. Protective coatings have also been proposed, notable a layer of aluminium on anode surfaces. Poor wet ability of carbon by the aluminium leads to problems in the uniformity of such coatings. Another proposed coating consists of alumina, but this has the disadvantage of creating thermal insulation around the anode leading to local overheating and acceleration of oxidation process.
Boron compounds in the form of B_2O_3 & H_3BO_3 have been found to inhibit the catalytic impurities by forming stable alloys therewith. Attempts to coat the anodes with Boron compounds have not been successful. As per US patent 3852 107 coating of 1-5 mm thick coating has been tried on the anode surface by spraying. Another attempt was made to coat the carbon body with a solution of ammonium pentoborate or ammonium tetraborate. This method was also unsuccessful. Later an impregnation method has been somewhat successful where the anode surface up to a certain height is immersed into a solution containing boron compounds.
Attempts have been made by NALCO R&D department to carry out experiments and plant trials by addition of Boric acid (H_3BO_3) in anodes.

2. Background

Calcined petroleum coke (CPC) has been used for more than 120 years to produce the carbon anodes used in the Hall-Heroult aluminium electrolysis process. Prebaked anodes are produced with 55–65% CPC, 13–15% coal tar pitch binder, and 20–30% recycled anode butts. The anodes are consumed at a net consumption rate of approximately 400 - 450kg carbon/ton aluminium for modern smelting cells. CPC is produced by heating or calcining green petroleum coke (GPC) at temperatures greater than 1200 degC. The production of GPC has remained essentially the same since 1929 when the modern delayed coking process was born. This was followed in 1935 by the development of the rotary kiln calcining process, which is the most commonly used technology in the Western world. The aluminium industry has had a ready supply of good-quality GPC and CPC for many years, but the situation has become more challenging over the last 10-15 years due to a general trend toward higher impurity levels resulting from changes in crude and refining economics.

The general trend has been an increase in trace metals like V and Ni and an increase in S levels.

The quality of CPC being supplied to NALCO differs mainly in apparent density & metallic impurities which is again dependant on the quality of green petroleum coke used in the calcining plant. High Vanadium in CPC affects the air reactivity of anodes and current efficiency of pots. Several technical papers have been published on this subject which explains the impact of changes in CPC quality on anode quality and smelter plant operation performance. Vanadium level in NALCO's CPC supplies vary in the range 0.002 to 0.025% Due to high vanadium levels in CPC, the air reactivity residue of anodes remains at the level of 60-65%.
Hence R&D dept has made this endeavour to find an adaptable method for improvement of air reactivity of anodes and made a trial at plant level to show the actual benefits.

3. Consumption of Anode carbon

In the electrolysis process the removal of oxygen evolved from the dissolution of alumina in the high temperature molten cryolite electrolyte, necessitates that carbon anode is consumed according to the stoichiometric reaction as shown in equation (1) at a theoretical rate of 334kgCarbon/T Aluminium. Typical current efficiencies of 90% & above, side reactions of carbon under the pot conditions raise this figure to 400-450 kg Carbon/T of metal.

9. Conclusion

It has been observed from the above trials carried out at smelter plant of NALCO that boric acid addition in anodes leads to improvement mainly the air reactivity residue of anodes, this will help in reduction of net carbon consumption keeping the boron content of metal within acceptable limits. Simultaneously there will be a reduction of greenhouse gas (CO_2) emission and thus carbon footprint of smelter plant. Air reactivity dust of anodes has also decreased by 8.9%. This will help in lowering the carbon dust and mushroom generation in the pots and thus improvement in current efficiency of pots.
Many aluminium smelters in the world are facing the problem of deteriorating CPC quality mainly due to increased levels of Vanadium, Nickel & Sulphur. The solution enumerated in this paper can be adapted in any smelter for lowering the air reactivity of anodes.

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