INFLUENCE OF PETROLEUM COKE SULPHUR CONTENT ON THE SODIUM SENSITIVITY OF CARBON ANODES

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ABSTRACT

Carbon anodes can contain significant quantities of sodium depending on the raw materials and recycled butts cleanliness. The extent of the catalytic effect of the sodium on the anode reactivity, i.e. the "sodium sensitivity", is dependant on the coke nature.

An investigation of a range of petroleum cokes was undertaken to study the influence of the sulphur on the sodium sensitivity. Besides the standard characterisation tests, a range of analytical methods was employed including Controlled Atmosphere Electron Microscopy (CAEM), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS) and Thermogravimetric Analysis (TGA).

The results of these investigations have been used to elucidate a mechanism to explain the sodium sensitivity.

INTRODUCTION

The raw materials used for the production of the dry recipe in prebaked anode plants are petroleum coke, crushed butts, green scrap and baked scrap. A binder, typically coal tar pitch, is added to coat the filler aggregate particles and ensure the compacted anode block maintains it's structural form.

Carbon anodes can contain significant quantities of sodium depending on the raw materials and recycled butts cleanliness. Sodium can be inherent in crude oil, or acquired during the drilling procedure. During oil refining and coking, the majority of the metals are deposited in the coke. Further sodium can be deposited on the coke while decoking the drum and after calcining if the purity of the water used for the cutting and cooling operations is not controlled.

Prior to tar distillation for pitch production the feedstock is dosed with controlled amounts of either a sodium carbonate or sodium hydroxide solution to neutralize ammonium chloride dissolved int he tar water[1]. This eliminates the problem of corrosion in the fractionating equipment due to chloride attack. Unfortunately the added sodium ends up in the pitch and subsequently the anode.

Spent anode butts are removed from the cell, cleaned and crushed before mixing with the pitch and coke to form the anode. A large level of the impurities present in the anode is concentrated in the butts. Butts may also contain impregnated cryolite (Na_3AlF_6) and bath material (a mixture of cryolite and alumina Al_2O_3) depending on the efficiency of the cleaning procedure. Dirty butts may contain as much as 12000 ppm sodium.

The extent of the catalytic effect of the sodium on the anode reactivity, i.e. the "sodium sensitivity", is dependant on the coke nature. R&D Carbon Ltd developed a bench scale procedure to quantify this which was presented in Light Metals 1991[2]. Figure 1 shows the influence of increasing sodium (dirty butts) content on the carboxy reactivity residue of full size anodes made out of two different petroleum cokes.

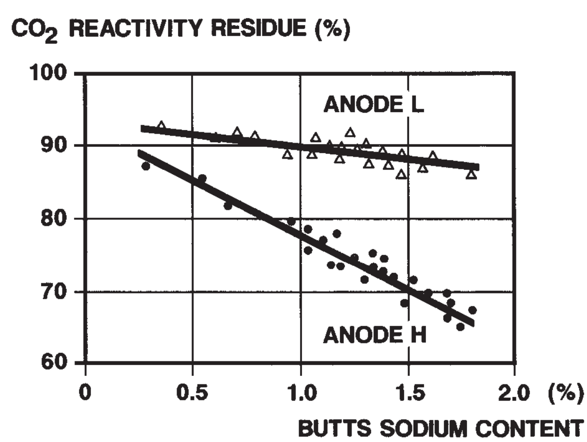

Figure 1. Influence of the butts sodium content on the carboxy reactivity residue of anodes.

There is a strong indication that the sensitivity of the cokes to dirty butts addition (i.e. their sodium sensitivity) is different. The photograph in figure 2 illustrates the large differences that can occur in anodes made with cokes having a similar granular carboxy reactivity.

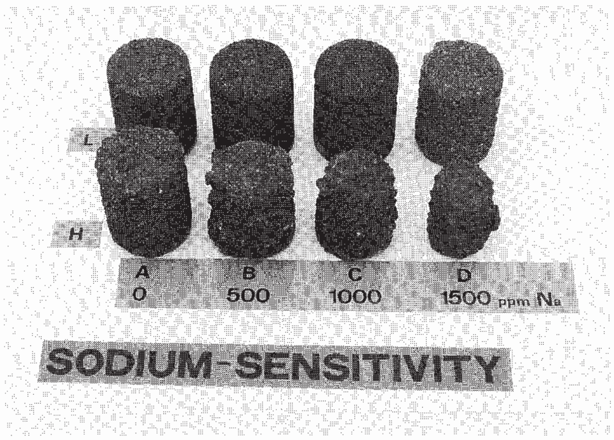

Figure 2. The carboxy reactivity residues of high and low sodium sensitivity cokes.

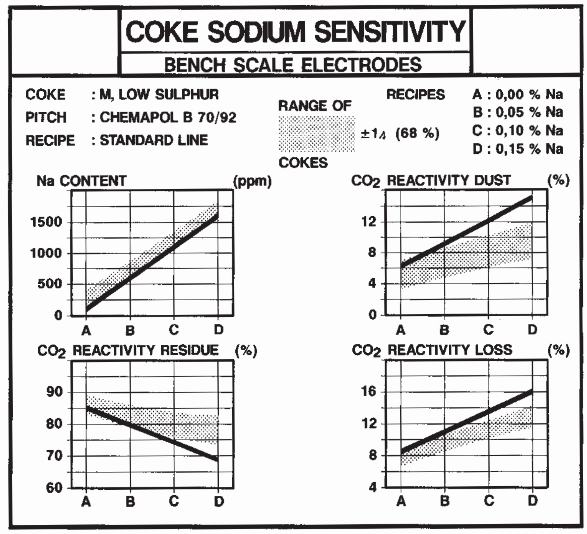

Figure 3. Bench Scale results for low sulphur coke M.

A comparison of the results of many such investigations led us to believe that the petroleum coke sulphur content had an important influence on the sodium sensitivity (other important parameters include the coke porosity, calcination degree and macrostructure). An investigation of two petroleum cokes with high or low sulphur but otherwise similar characteristics was undertaken to study the influence of the sulphur content. Besides the standard characterization tests, a range of analytical methods were employed.

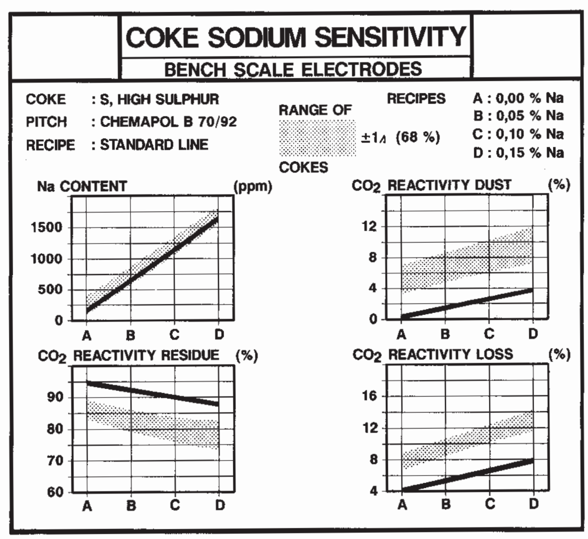

Figure 4. Bench scale results for high sulphur coke S.

BENCH SCALE PROCEDURE

Bench scale electrodes containing increasing levels of sodium contamination were prepared according to the procedure of Fischer and Perruchoud[2]. The bench scale results for typical low (labelled M) and high (labelled S) sulphur cokes are shown in figures 3 and 4 respectively.

It is evident that the sensitivity to sodium additions is much greater for coke M, ie the catalytic activity of the sodium is much greater in the absence of sulphur.