Vanadium Speciation in Petroleum Cokes for Anodes used in Aluminium Electrolysis

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Abstract

The expanding aluminium industry is facing challenges with availability in raw materials. A wider range of petroleum cokes are being taken into use, blurring the border between anode grade and fuel grade coke in anode production. Vanadium, a common impurity in coke, is known to be a catalyst for air-reactivity burn-off, which may increase the consumption rate of the anodes. Additionally, vanadium is an unwanted impurity in the finished aluminium. Levels of vanadium and sulfur are typically correlated in petroleum cokes, but as vanadium is present mostly as porphyrins in crude oil, it is assumed this is the case in the resulting coke as well, rather than as vanadium-sulfur compounds. In this work the actual speciation of vanadium was investigated using X-ray absorption spectroscopy techniques. Six different industrial cokes were characterized with XANES, and they all seem to have the approximate same vanadium speciation. Based on the comparison with different vanadium reference standards, it was shown that vanadium is not present as the previously anticipated porphyrin. Based on the EXAFS spectrum, bonds between vanadium and sulfur were identified. Close to identical speciation of the vanadium was found in all the cokes, and this was reflected in a linear increase in air reactivity with vanadium content.

Keywords: Petroleum coke, X-ray absorption spectroscopy, vanadium speciation, air reactivity.

1. Introduction

Carbon anodes are used in the only commercially available method for producing aluminium, the Hall-Héroult process [1]. In modern cells, pre-baked anodes with a lifetime of 25-30 days are used. The remaining anode butt is cleaned and recycled to be used in the production of new anodes. Green anodes are made by mixing calcined petroleum coke (CPC) and recycled butts together with coal tar pitch, and the formed anodes are stacked within an anode baking furnace and exposed to three-week heat treatment. As it is important to have a dense, stable and unreactive anode to achieve stable performance in the cells, anode smelters have strict requirements concerning the CPC quality. This includes bulk and real density, particle size, thermal expansion coefficient, sulfur and trace metal impurity content. All these properties have an impact on the process [2]. Because the carbon anode is consumed during the electrolysis, cost is also a consideration, meaning that very high quality and expensive coke material is unfavourable. Since petroleum coke is a by-product from the petroleum refining process, both quality and price of the coke depend on this industry rather than the aluminium industry, although a high demand from the aluminium industry may drive the price upwards.

A change in raw material quality due to changes in the petroleum industry and increased demand for anode grade coke has resulted in the need for the aluminium industry to investigate the effect of lower quality coke in anode production. Readily available coke is likely to be less dense and have more sulfur and trace metal impurities than conventional anode-grade cokes, which is believed to increase reactivity of the anode and reduce the anode stand time. Smelters have specifications on sulfur and content of vanadium, nickel, calcium, iron, silicon and sodium. These metals originate both from the precursors of the coke, and, for sodium, calcium and iron, also from the bath residue in the butts. Acceptable sulfur levels are decided based on law enforcement regarding emission of SO_2 from the plant, although smelters in some countries with strict restrictions on sulfur emissions have installed wet scrubbers. Several of the metal impurities end up in the finished aluminium, and thus the specification is determined based on the corresponding requirements of the aluminium alloys. Sulfur is in the quantity of percent rather than the metal traces of ppm, and a higher sulfur level usually also results in a higher metal impurity level. A linear correlation between sulfur and vanadium is usually observed in green coke [3], which indicates that a higher toleration of sulfur, usually obtainable by SO_2-scrubbers, also will include an increase in the level of vanadium.

Several of the impurities are known to catalyse reactions between the carbon anode and air or CO_2. Vanadium is known to be a strong catalyser for the airburn reaction at elevated temperatures, which can cause problems if any of the anode surface is exposed to air. To avoid airburn the anode is covered with anode cover material, usually alumina. In modern cell operation the airburn is reduced due to good covering practice, but still not insignificant. The effect of vanadium on carboxy reactivity is believed to be low or moderate, but as sulfur is believed to lower this reactivity the exact effect is difficult to determine [4]. The metals are usually present in the crude oil as organometallic complexes [2], which are soluble in the crude and tend to concentrate in the residual streams and thus in the coke by-product rather than the high end products. It is believed the metals are still in this form in the coke. Vanadium is believed to be in the form of porphyrins in the coke due to its presence in the crude oil [5], but there have been little to no investigations into vanadium speciation in cokes.

X-ray absorption spectroscopy (XAS) techniques can be used to investigate speciation in many materials. Coals, chars, cokes and other organic matter have been investigated for sulfur speciation using X-ray absorption near edge spectroscopy (XANES) [6-12], but because of the low quantity of vanadium compared to sulfur, any vanadium-sulfur species will not be identified when investigating sulfur. A review of K-edge XANES of a number of vanadium compounds was done by Wong [13] in 1984 revealing a number of trends observed for the vanadium spectra, but the use of the technique to investigate carbon materials did not begin until several decades later. Duchesne [14] investigated oxidation states of V in petroleum coke gasification samples by XANES and revealed the expected differences in oxidation state from feed to by-products, but the exact specification presented here only included oxides and not organic complexes. Oil sands fluid petroleum cokes were investigated by Nesbitt [15], and using µXANES V(IV) revealed porphyrins and octahedrally coordinated V(III) were the major vanadium components.

In this work, XAS techniques are used to study six calcined petroleum cokes to determine vanadium speciation. XANES is used to identify differences between the cokes, as well as recognize the oxidation state of V. Vanadium porphyrins and vanadium sulfides could be identified by comparing the spectrum of the cokes to known vanadium reference species. The extended X-ray absorption fine structure (EXAFS) is then used to identify the probability of

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6. References

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