

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

bonding to different atoms. Finally, any correlations of the speciation of vanadium with air reactivity are also investigated.

2. Experimental

Six industrial CPC samples were chosen from a larger selection based on sulfur and vanadium content (determined by X-ray fluorescence), and how close the structure was to regular anode coke regarding isotropy and texture. Five cokes were anisotropic with close to typical anode coke texture, while one coke was isotropic with fine mosaic texture. Three of the anisotropic cokes had a linear relationship between sulfur and vanadium, while the last two have either higher vanadium or sulfur than the linear trend. Data for the chosen cokes is presented in Table 1. Pilot scale anodes were made using 100 % of each coke, and the anode air reactivity was measured on small test pieces using a thermogravimetric analysis method similar to ISO 12989-2:2004. Except for coke F, all the anodes were investigated for air reactivity.

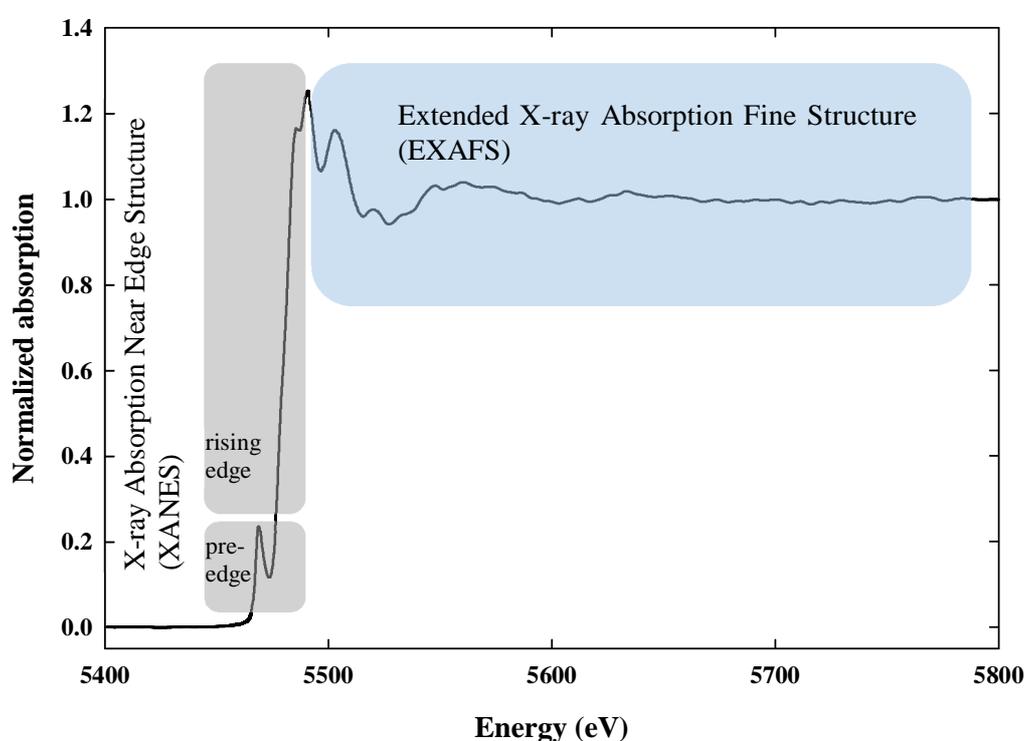
Table 1. Composition the six cokes. Sulfur (S), vanadium (V) and total metal (M) content were measured on coke material using XRF. M include Na, Mg, Al, Si, Ca, V, Fe and Ni.

	S (%)	V (ppm)	M (ppm)	Notes
Coke A	1.42	116	761	Anisotropic
Coke B	3.56	402	1323	Anisotropic
Coke C	5.54	432	1356	Anisotropic
Coke D	3.86	714	1668	Anisotropic
Coke E	4.42	624	2009	Isotropic
Coke F	4.76	541	2861	Anisotropic, very high M, no air reactivity measurements performed

XAS was performed at the Australian Synchrotron using the XAS beamline in fluorescence mode. All six cokes were investigated at the vanadium K-edge, as well as the eight vanadium reference standards presented in Table 2 including vanadium foil. The reference standards were purchased from Sigma Aldrich, with the exception of V_2S_3 purchased from American Elements. The samples were ground and mounted in sample holders and loaded into the specimen chamber. The reference standards were mixed with cellulose to a concentration giving a good signal, 5000 ppm for most standards, before mounting and loading. From -10 eV to +50 eV around the K-edge (around 5465 eV) the steps were 0.25 eV, however, a larger step size was used before and after this region. The vanadium K-edge XAS spectra were processed using Athena software [16], and analysis done on the averaged spectra of three scans. All spectra were normalized by defining the signal before the pre-edge to 0 and the signal in the post-edge region to 1, and these two regions will then be presented as two parallel lines. XANES is the region within ~50 eV from the edge, and the EXAFS region is at higher energies, with an example presented in Figure 1. The EXAFS region was investigated using the Artemis software by fitting known crystal data to the experimental spectra.

Table 2. Vanadium reference standards, concentration of V obtained by mixing with cellulose, and oxidation states.

Standard	V concentration, mixed with cellulose (ppm)	Oxidation state
Vanadium foil	-	0
V ₂ O ₃	5000	+3
VO ₂	5000	+4
V ₂ O ₅	5000	+5
V ₂ S ₃	5000	+3
VC	3333	+4
5,10,15,20-Tetraphenyl-21H,23H-porphine vanadium(IV) oxide	2000	+4
VOSO ₄	5000	+4

**Figure 1. XAS spectrum for vanadium dioxide (VO₂).**

The energy calibration from the transmission data on the foil was evaluated and it was found that the beamline was very stable in energy between scans and no corrections were needed.

3. Results and Discussion

3.1 XAS

The vanadium reference standard XAS spectra are presented in Figure 2. The rising edge moves to higher energies with a higher oxidation state, clearly visible for the oxides in (a), and the similar oxidation state of the standards in (b) show the rising edge at approximately the same energy level. V³⁺ and V⁴⁺ are known to have an overlap (as well as V⁴⁺ and V⁵⁺) at higher energies. The distinct vanadium pre-edge can be observed in all standards except for V₂O₃. This is consistent with previous data [13].

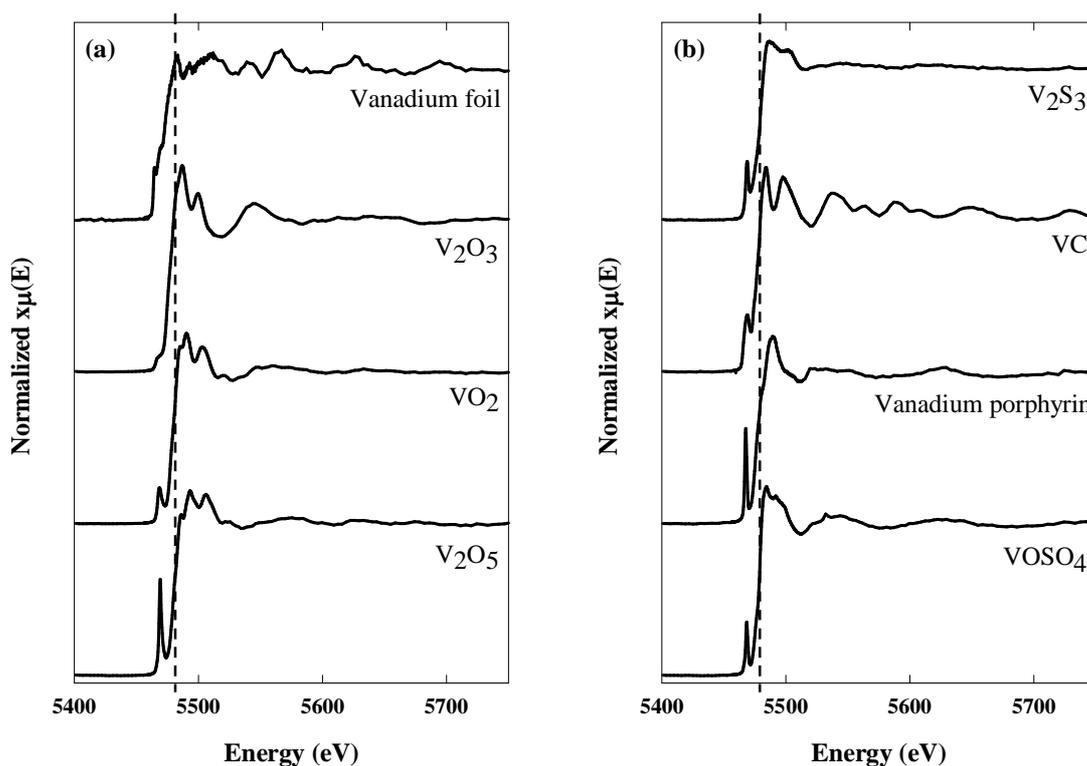


Figure 2. Vanadium K-edge XAS spectra for reference standards, (a) the vanadium foil and vanadium oxides, and (b) vanadium sulfide, carbide, porphyrin and vanadyl sulfate.

The coke XAS spectra are presented in Figure 3, and the similarities between the graphs indicate that the vanadium speciation is similar in all six cokes. A pre-edge peak, more visible in Figure 3b, is observed at 5467.5 eV. For this peak the intensity was higher for cokes A, B and D than C, E and F. None of the standards in Figure 2 had a pre-edge in this region, or an edge at these low energies, besides V foil with a pre-edge at 5464.5 eV.

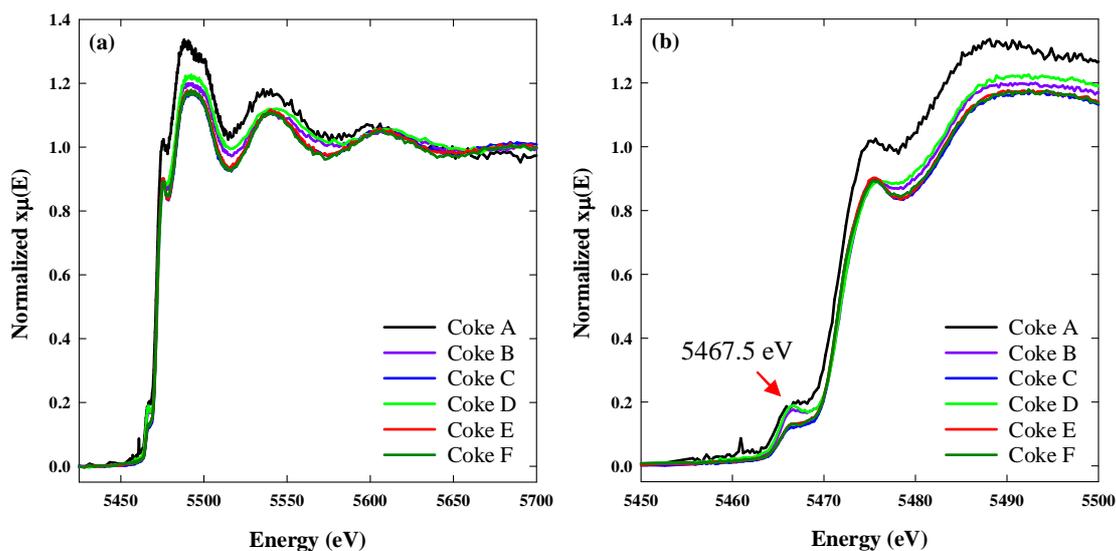


Figure 3. The vanadium K-edge XAS spectra for six industrial cokes. (a) XANES and EXAFS region and (b) XANES region only.

The edge position, located at 5471-5472 eV, is about the middle of the steep rising part, or the peak maximum of the derivative spectrum illustrated for coke D in Figure 4a (the first peak in this spectrum is the steepest part of the rise of the pre-edge, sometimes called the threshold). All the references have the edge above this value. Vanadium foil has the closest value at 5473 eV, but the pre-edge is wrong, and the general shape of the XAS spectrum is very different from the cokes' shape. Furthermore, VC has an edge a little higher than V foil, and the other references investigated in this study, including the vanadium sulfide and vanadium porphyrin, are 5-15 eV higher than the K-edge of the coke. A comparison between coke D and some of the standards is presented in Figure 4b show the differences better.

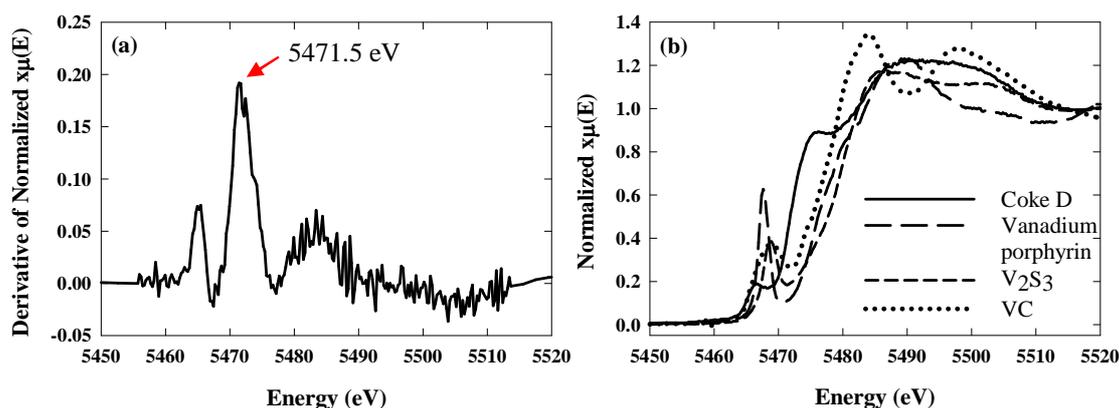


Figure 4. (a) The derivative spectrum of coke D and (b) XANES region of coke D and some reference standards.

While an XANES analysis yielded some information on vanadium speciation in the cokes, an EXAFS analysis can provide additional information on the structure and chemistry of the vanadium bonding. A preliminary EXAFS analysis suggests that the V is present as a vanadium sulfide, of which there are many possible forms. A detailed analysis will be conducted, but is outside the scope of this paper. So far it can be concluded that V_2S_3 is not the correct compound.

3.2 Evaluation of Catalysed Air Reactivity Burnoff

Air reactivity increased with increasing vanadium and metal content, as presented in Figure 5. The difference between the graphs indicates that vanadium, the metallic element most abundant in the cokes, is most likely the element with highest effect on this factor. Note that coke E, with highest total metal content, as shown in (b), has a lower reactivity than coke D which has the highest vanadium content. It appears to be an approximate linear relationship between airburn and vanadium content, with coke C deviating a little from this trend. All measurements on the anodes from coke C were practically identical, giving almost no error bar on this point, while the measurements on coke D had the largest variations.

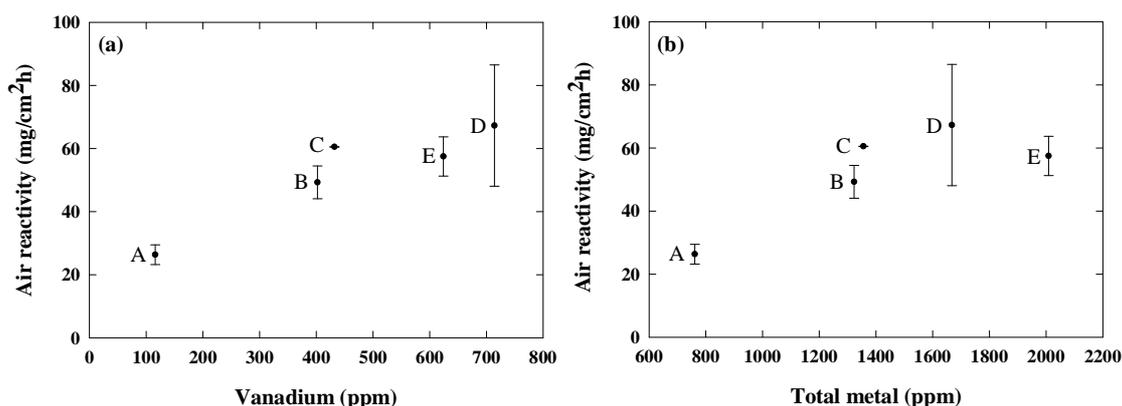


Figure 5. Air reactivity for anodes made of the cokes concerning (a) vanadium and (b) total metal content.

It is well known that vanadium is a strong catalyst for the reaction between air and carbon at the operating temperatures of electrolysis cells, something this study also shows. Despite the large uncertainty in the reactivity measurements of the anode made from coke D, the fact that this has higher reactivity than coke E, with more total metal can be taken to further illustrate the strong catalytic effect of V. Overall, these are indications that vanadium is most likely the element with the highest contribution to mass loss due to airburn. Iron is also known to be a strong airburn catalyst, and part of the high total metal content is from a doubling of this trace metal impurity in this coke, as well as much more of Al and Si, which effects are believed to be less than vanadium and iron, although not classified as weak. The XAS results showed no difference in speciation, meaning the catalytic effect of V is not a speciation dependent property. A coke with high vanadium content is expected to have higher mass loss due to reaction between air and carbon than a coke with lower vanadium content.

4. Conclusion

Characterizing the cokes with XAS showed that the six industrial calcined petroleum cokes in this study, with vanadium content varying from 100 to 700 ppm, had the same vanadium speciation. Based on the XANES results, the previously reported vanadium porphyrin is excluded as a compound, while the preliminary EXAFS analysis shows that it is most likely vanadium in a sulfur compound that is present in these cokes. This is in good correspondence with the well known observation that vanadium and sulfur content have a significant positive correlation in cokes. The air reactivity is not a large problem during use of carbon anodes during aluminium production, however a higher reactivity correlates with higher vanadium content, which is not a speciation dependent property.

These cokes have been considered for use as anode raw material. Further understanding of how the type of vanadium bonding influences the air reactivity is clearly of interest when evaluating the risks and additional loss of materials of using these raw materials.

5. Acknowledgement

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