An EXAFS and XANES Study of V, Ni and Fe Speciation in Cokes for Anodes Used in Aluminium Production

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ABSTRACT

Lower quality petroleum coke is required to be used in anode manufacture containing S and the metal impurities V, Ni and Fe. These affect the anode performance in the aluminium production process. The chemical identity of the metal species in the coke is not known. Industrial petroleum cokes with high S and containing V, Ni and Fe were analysed by XANES and EXAFS. XANES spectra were compared with standards. EXAFS was used to compare the impurity metal structures with known crystal structures. V is present largely as hexagonal V_3S_4. Ni is present largely as hexagonal NiS. Fe is present as hexagonal FeS.

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These compounds all have only short range order, suggesting they are highly dispersed in the coke matrix. This knowledge of the chemical state of the metal elements in coke, which are known to affect anode performance, is the first step in understanding the mechanism of action of these elements on anode reactivity.

1. Introduction

The Hall-Héroult process of producing aluminium by electrolysis of aluminium oxide using carbon anodes in a cryolite melt is the only commercial method to produce aluminium[1]. The global increase in production of the metal results in a higher consumption of the raw materials. The consumable carbon anodes are made from calcined petroleum coke (ca. 70%), recycled anode butts (ca. 15%) and coal tar pitch (ca. 15%). The formed anodes are stacked within an anode baking furnace and exposed to a three-week heat treatment. To achieve a predictable and effective behaviour in the cell there are strict requirements on the calcined petroleum coke (CPC) quality. However, because of the increase in demand, combined with changes in the petroleum industry from which coke is a by-product, the quality of the coke available for use in pre-baked anodes is decreasing[2]. The aluminium industry now needs to determine the impact on the smelting process of using lower quality cokes containing higher metal and sulfur content and lower density, which are closer to the quality of fuel grade coke.

Higher levels of impurities in the coke may result in changes in the smelter operations, like changes in anode performance and cell performance (current efficiency) and changes in primary metal purity[3]. An important aspect of anode performance is the unwanted chemical reactions between the carbon anode and air (airburn) or the produced CO_2 (carboxy reactivity). Both of these reactions increase carbon consumption undesirably. More noble

metals than aluminium, such as V, Na and Fe, can be electrochemically reduced before aluminium, lowering the current efficiency and increasing the carbon consumption. This also results in the reduction of the primary aluminium quality because the impurities end up in the tapped hot metal.

Some metal impurities have been shown to catalyse airburn or the CO_2 reaction[3]. Vanadium is always present in crude oil and becomes concentrated in the heavier fractions and therefore in the petroleum cokes, typically at a level of several hundred ppm in the coke. Vanadium has been shown to be an active catalyst for the CO_2 reaction of anodes at elevated temperatures[4]. Nickel is another impurity normally present in poor quality cokes at similar levels to V and has been shown to have a negative effect on both air and carboxy reactivity[4, 5]. A third metal, iron is also present in cokes, and may be derived from the crude oil or introduced inadvertently during processing [6]. Fe is an active catalyst for airburn and the CO_2 reaction[7]. Sodium, which is not very abundant in the cokes but can enter the anodes from the use of butts[8, 9], and other metals that occur in coke in lesser amounts can also affect these reactions. To avoid airburn the anode is covered with anode cover material, usually alumina. In modern cell operation the airburn is limited due to good covering practice, but is still not insignificant. The reaction with CO_2 is more difficult to control, as it occurs when the electrochemically produced CO_2 diffuses into the anode and reacts.

Sulfur also tends to increase with increasing metal impurities in poorer quality petroleum coke. It is believed to have a desirable inhibiting effect on the carboxy reactivity[10, 11], so portions of high sulfur coke are often blended in to reduce this reactivity. The nature of the inhibiting reaction is not known. Despite sulfur's positive effect on the carboxy reactivity, too high levels of S are unwanted because they leave the cell as environmentally unfriendly gases. In CPC in some cases sulfur has been observed as a thiophene-containing polycyclic aromatic hydrocarbons[12-15]. In the high sulfur cokes studied here for metal impurities, a

previous study has shown that the sulfur is present as elemental sulfur or at least contains S-S bonds [16]. These cokes did not follow the normally accepted trend of decreasing CO_2 reactivity with increasing sulfur content.

X-ray absorption spectroscopy (XAS) consisting of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS or XAFS) is a very powerful technique for identifying chemical speciation in solid state materials. XANES is normally used as a fingerprint method to compare the shape of the absorption edge region of standards to samples with unknown chemical structure. EXAFS is essentially a crytallographic structure technique (or pair distribution analysis), where known structural forms (normally obtained from X-ray diffraction) may be fitted to the EXAFS of the unknown samples to determine the likely crystal structure. It has the very substantial advantage over X-ray diffraction techniques for crystal structure in that the structure of interest may be very dilute and highly dispersed and still be tractable by EXAFS. The metals V and Ni are present in crude oil in large part as soluble organometallic complexes such as porphyrins where the metal is coordinated to N [17-19] and also non-porphyrin organic complexes where the metal is coordinated to S or O [20] [21]. The metals concentrate in the heavy fractions and thus in the coke by-product rather than the light fractions. Less interest has been taken in the nature of Fe in crude oil.

In this study X-ray absorption spectroscopy (both XANES and EXAFS) is used to investigate the chemical speciation of the metals vanadium, nickel and iron in industrially produced petroleum cokes with varying levels of these metals and sulfur, different structures and CO_2 reactivity. These are cokes with the impurity level occurring naturally (not by doping), for which reactivity data is available and major sulfur speciation is known. Insights are sought in the chemical structure of catalytically active impurities and the relationship of these impurities to anode performance.

2. Experimental section

2.1 Coke selection

A large number of industrial calcined petroleum cokes originating from different crude oils and produced by different manufacturers were analysed by X-ray fluorescence spectroscopy (XRF) according to ISO 12980:2000 for metal and sulfur content. From the cokes available a selection of six coke samples were chosen for this work based on sulfur and vanadium content to give a range of V and S content. Cokes A-E are the same as those used in a recent XANES study by the same authors of the sulfur speciation in these cokes [16], where sulfur speciation using XANES were accomplished, and evaluated to CO_2 reactivity and structure. Cokes A-D, and the additional F, are anisotropic in nature similar to regular anode coke, while coke E is isotropic. The S, V, Ni and Fe composition for each of the six selected petroleum cokes samples is detailed in Table 1.

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

	S (%)	V (ppm)	Ni (ppm)	Fe (ppm)
Coke A	1.42	116	192	178
Coke B	3.56	402	210	264
Coke C	5.54	432	192	316
Coke D	3.86	714	426	156
Coke E	4.42	624	323	464
Coke F	4.76	541	234	724

2.2 XAS measurement and analysis

The cokes were ground finely (< 45 μm) with a mortar and pestle, without dilution, before mounting for XAS as packed powders in standard polymer sample holders.

X-ray absorption spectra were recorded on the XAS beamline at the Australian Synchrotron, Victoria, Australia. The energy was controlled using a fixed exit Si(111) double crystal monochromator. The beam was conditioned using a collimating mirror (Si) and a toroidal focusing mirror (Rh coated). Higher harmonics were rejected using these two mirrors and a flat harmonic rejection mirror (SiO_2). Spectra were recorded in fluorescence mode using a 100 element Ge pixel array fluorescence detector. The X-ray beamsize on the sample was approximately 1 x 1.5 mm. The energy scale was calibrated by simultaneously measuring a metal foil (V, Ni or Fe) placed between two downstream ion chambers.

XAS spectra were recorded around the K-edges of Fe, Ni and V at room temperature. Samples were packed in 1 mm thick poly(methyl methacrylate) sample holders.

A number of reference standards for each element were also run with the intention to use these for XANES analysis and to enable an experimental value of the amplitude reduction factor, S_0^2, from similar chemical structures for fitting of samples to EXAFS models. The reference materials were diluted with cellulose powder to suitable concentrations of the element and ground finely (Table 1). Data was collected to be suitable for both XANES and EXAFS analysis, with variable energy steps and constant dwell time. Pre-edge data was collected at 0.003 eV energy intervals, around the edge at 0.00025 eV intervals, above the XANES region at steps of k = 0.07 Å^{-1} steps up to k = 10 Å^{-1} above the edge with a dwell time of 1 s at each step.

Table 2. Concentration of V, Ni and Fe reference standards obtained by mixing with cellulose

Material	Concentration (ppm)	Producer
Vanadium		
Vanadium foil	-	
V_2O_3	5000	Sigma Aldrich
VO_2	5000	Sigma Aldrich
V_2O_5	5000	Sigma Aldrich
V_2S_3	5000	American Elements
VC	3333	Sigma Aldrich
2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine vanadium(IV) oxide	2000	Sigma Aldrich
$VOSO_4$	5000	Sigma Aldrich
Nickel		
Nickel foil	-	
NiO	1000	Sigma Aldrich
Ni_3S_2	1000	Sigma Aldrich
2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine nickel(II)	1000	Sigma Aldrich
Iron		
Iron foil	-	
FeO	10000	Sigma Aldrich
Fe_2O_3	1000	Sigma Aldrich
Fe_3O_4	1000	Sigma Aldrich
$FeSO_4 \cdot 7H_2O$	1000	Will find out
FeS	10000	Sigma Aldrich
FeS_2	10000	The Crystal People, Christchurch, New Zealand
Fe_3C	15000	American Elements
5,10,15,20-Tetraphenyl-21H,23H-	1000	Sigma Aldrich

porphine iron(III) chloride		

Processing for XANES used the Athena software [22]. Analysis was performed with the averaged spectra of at three scans for V, two or three for Fe, while only a single scan was obtained for the Ni measurements.

To the Ni and Fe XANES spectra of the cokes linear combination fitting (LCF) of normalized $\mu(E)$ spectra of reference compounds was performed with Athena software. The X-ray edge position, E_0, was held to be the same for all components. Non-linear least squares minimization was used for fitting and was carried out over an energy range 20 eV below E_0 to 50 eV above E_0. After initial screening of the reference spectra with the coke spectra the final LCF's used a combination of the most promising reference compounds. Linear combination fits were tested with both normalised $\mu(E)$ and derivative $\mu(E)$.

The EXAFS region for V, Ni and Fe were processed using Artemis software[22] and fitted to crystal data from the crystallography open database[23] after removal of a glitches in the V K-edge at 5727 eV. A glitch was also present for the Ni K-edge at 8650-8660 eV but this region of the EXAFS spectrum ($k > 9$ Å^{-1}) was not used in the fitting as it had poor signal to noise.

EXAFS fitting was carried out in each of k, k^2, k^3 and R space, with similar results obtained in all of these. The results reported here are fitting in R (with k^2). The XAS data were recorded to $k = 10$ Å^{-1} but the higher energy data were not of sufficient quality for useful fitting (as judged by visual inspection), so fitting was terminated at lower k, typically around 8 Å^{-1}. The goodness of fit was determined by the EXAFS R-factor and by a visual inspection of the matching of the shape of the fit compared with the data. Importantly the value of S_0^2 obtained from an unconstrained fit was required to be in a realistic range, and

similar to that for the fit to a standard of a similar composition. The crystallographic structures for a variety of possible compounds were tested against the data for the cokes.
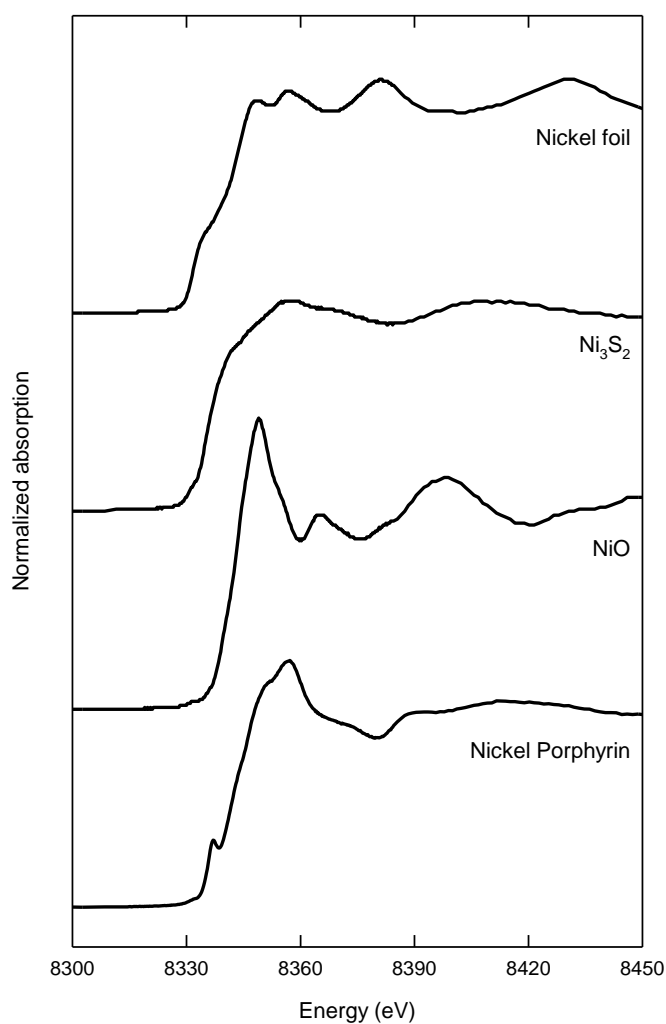
2. Air reactivity

Air reactivity was measured on anodes prepared from the cokes using thermogravimetric analysis similar to ISO12989-1.

3. Results and discussion

3.1 Nickel XANES

The reference compounds for Ni XANES display very significant differences in both the edge energy and the shape (Fig. 1).

Figure 1. The normalized absorption nickel K-edge XANES spectra for the reference compounds.

The Ni K-edge XANES of all five cokes appear similar. The coke D spectrum is presented here because it has the highest level of Ni in these cokes and therefore the best signal to noise in these spectra (other data is available in the Supplementary data file).

Matching of the Ni K-edge XANES to the dataset of measured compounds gave the best fit, for a single component, to Ni_3S_2 (Fig. 2). However, the fit is improved if a linear combination fit of Ni_3S_2 with nickel porphyrin is used (Fig. 3). Nickel porphyrin is used as an approximate representation a range of possible of nickel organic complexes. All the cokes

were similar but any subtle differences between the different cokes can be accommodated by varying the proportions of Ni_3S_2 and nickel porphyrin, particularly the fit at the main edge (Supplementary data, Table x, Fig. x). Other combinations of reference spectra gave poorer fits.
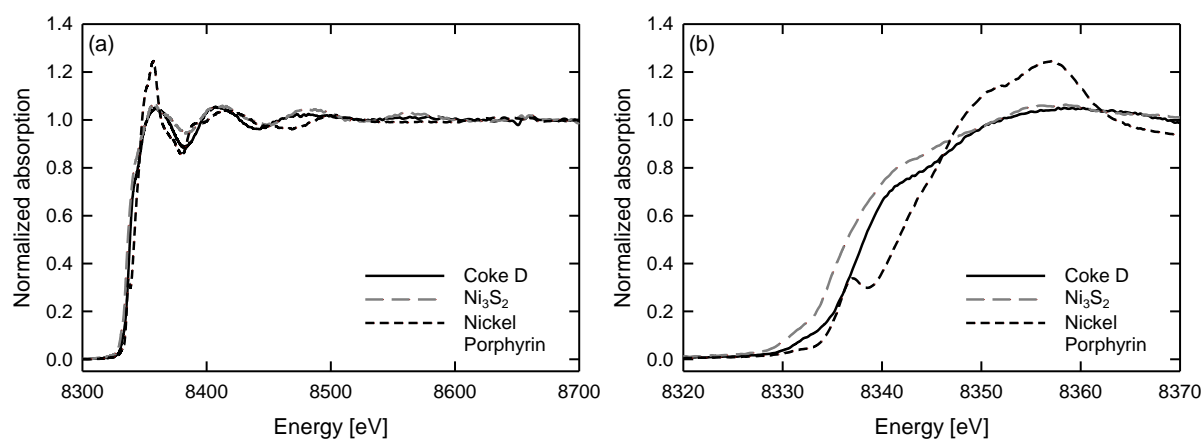
Figure 2. The normalized absorption nickel K-edge XANES spectra for industrial coke D with reference spectra nickel porphyrin and Ni_3S_2. (a) Whole energy region; (b) edge region.

The limitation of XANES must be recognized though. Comparison of the sample spectra are possible only to the reference spectra available. These reference spectra may not include compounds that are identical to those in the sample, and therefore a perfect match may not always be obtained. However, it would normally be expected that compounds with similar chemistry (oxidation state in particular) may have similar XANES spectra, particularly at the edge and this gives some confidence that the form of Ni present is similar to a nickel sulfide.
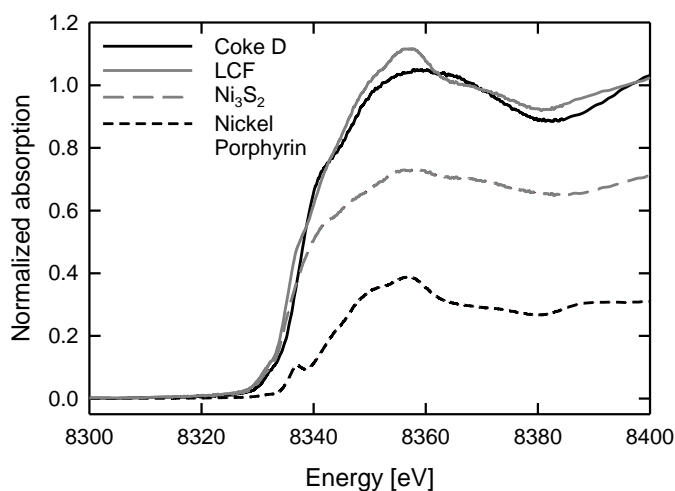
Figure 3. The linear combination fitting of the normalized absorption nickel K-edge XANES spectra with Ni_3S_2 (0.688) and nickel porphyrin (0.312) to coke D. R-factor 0.0092.

The XANES analysis for Ni therefore suggests that the nickel may be present as a sulfide or a complex organic sulfur compound or a mixture of the two. While there is some variation in the proportion of each of these between the cokes, the best fit for all of the cokes is to just these two components.

3.2 Nickel EXAFS

The Ni K-edge EXAFS data from the cokes was tested against a range of possible structures (Table 3). Two stoichiometries, NiS and NiS_2 gave satisfactory fits. Ni_2S_3 did not fit well to the experimental data. The best fit was hexagonal form of NiS (Fig. 4). Fitting was much improved by supposing there is only short range order. This suggests that the Ni is highly dispersed, and does not form crystals with long range order in the coke.

Table 3. Crystal structures tested for fit to the EXAFS of the cokes.

Compound	COD ID	Space	Crystal

		group	system
NiS	1010435	P6$_3$/mmc	Hexagonal
NiS	1011038	R3m:R	Trigonal
Ni$_3$S$_2$	1011250	R32:3	Trigonal
NiS$_2$	1544738	Pa-3	Cubic
NiO	1010093	Fm-3m	Cubic
Ni$_3$C	1528750	R-3c:H	Trigonal
Ni	9013024	Fm-3m	Cubic

Other possibilities considered plausibly present in coke, including NiO, Ni$_3$C and Ni, did not give good fits, with either unrealistic S_0^2 values (which should be close to 1), large ΔE_0 (> 5) or poor (high) R-factors.

The EXAFS analysis indicates a sulfide in the cokes with bond lengths similar to primitive hexagonal NiS.
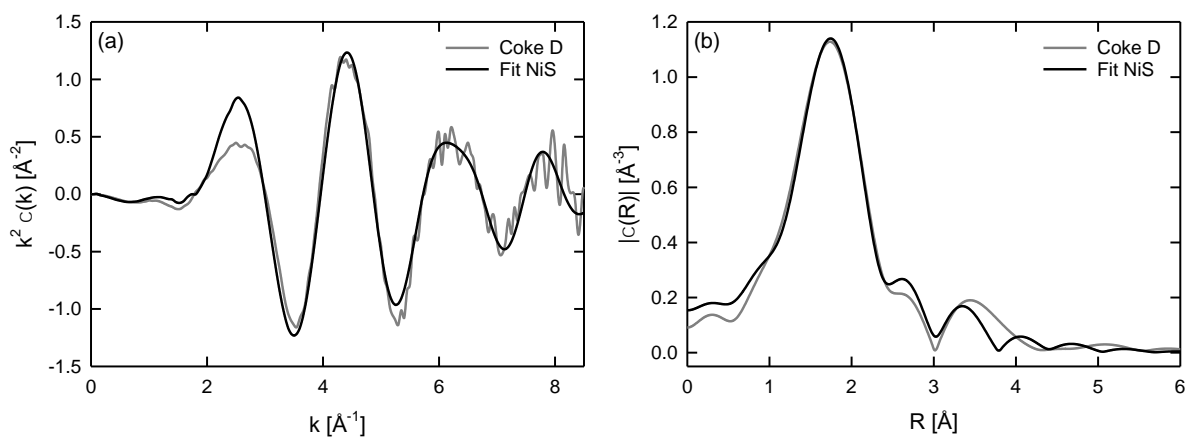

Figure 4. The experimental EXAFS spectrum for coke D and the FEFF model fit for hexagonal (P63/mmc) NiS fitted for k from 3 to 8 Å^{-1} in (a) k^2-space and (b) R-space. R-factor = 0.014, S_0^2 = 1.08, ΔE_0 = 0.08 for paths <4.1 Å.

So in summary, the Ni XANES suggested a nickel sulfide with possibly some admixture of porphyrin, while the EXAFS analysis indicates the cokes contain a sulfide with a structure similar to NiS primitive hexagonal P63/mmc with short range order.

3.3 Vanadium XAS

The reference compounds for V XANES display significant differences in the shape and a pre-edge feature although not a large change in the edge position (Fig. 5).
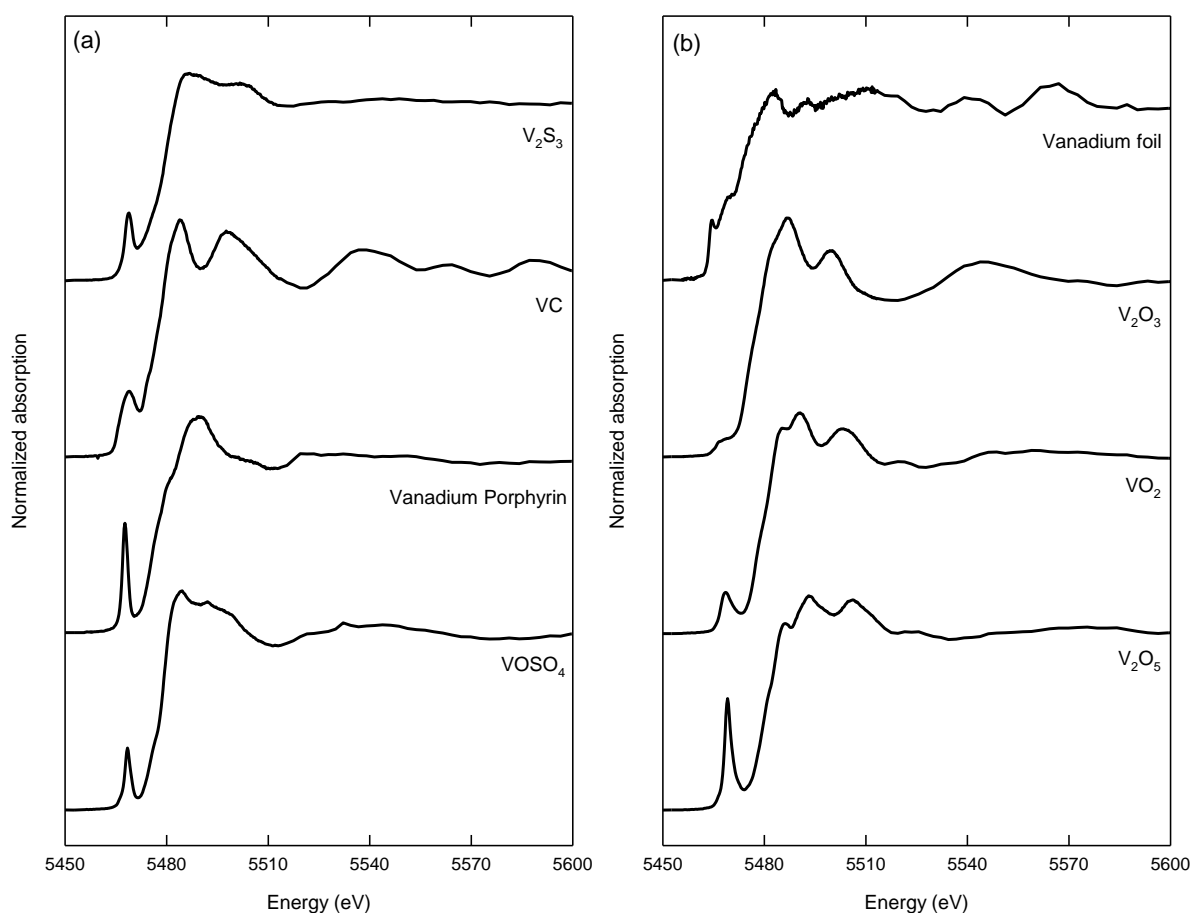
Figure 5. The normalized absorption vanadium K-edge XANES spectra for the reference compounds.

The V K-edge XANES of all five cokes appear similar. The Coke D spectrum is presented here because it has the highest level of V in these cokes and therefore the best signal to noise

in these spectra (other data is available in the Supplementary data file). Comparing the observed pre-edge and edge position of the V K-edge spectra for cokes with the spectra for the reference standards (Table 1) showed that none of the investigated references was a good fit (Fig 1b). All the cokes gave similar V K-edge XANES [24].
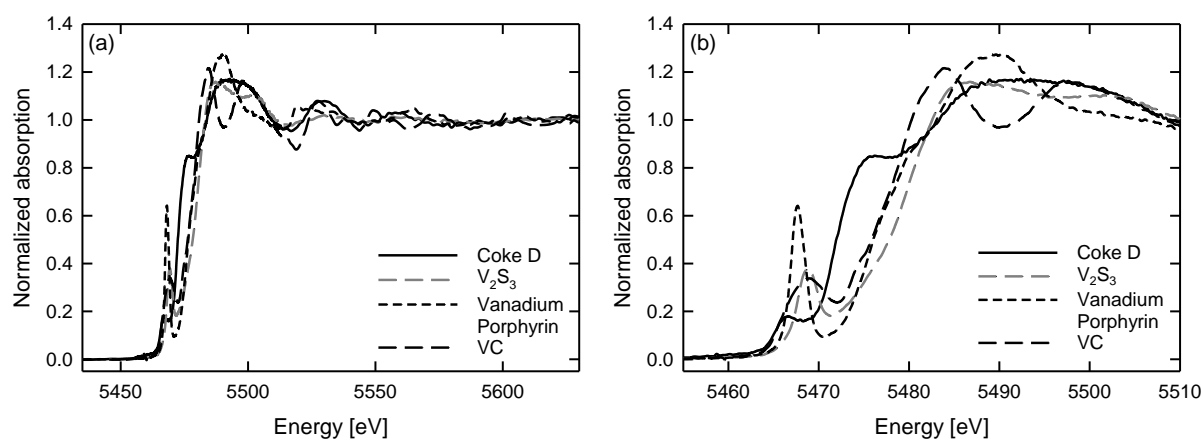
Figure 6. The normalized absorption vanadium K-edge XAS spectra for industrial coke D with reference spectra of VC, vanadium porphyrin and V_2S_3. (a) Whole energy region; (b) edge region.

A pre-edge peak is observed in the spectra of the cokes at 5466.6 eV while in the reference compounds, this pre-edge occurs at 2-3 eV higher energy. The main edge, located at 5471.1-5471.9 eV (for the peak of the derivative) in the cokes occurs 6-11 eV higher in the reference compounds (except V metal). Therefore there is no good match between the XANES spectra of the cokes and the reference standards selected. However, it is possible to be confident from the XANES data that the vanadium speciation is the same in all the cokes.

3.4 Vanadium EXAFS

The EXAFS region for the V K-edge of each coke was modelled for a variety of vanadium structures (Table 4).

Table 4. Crystal structures tested for fit to the EXAFS of the cokes.

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| Compound	COD ID	Space group	Crystal system
V_3S_4	2001606	$P6_3/m$	Hexagonal
V_3S_4	1537894	C1 2/m 1	Monoclinic
VS	1010579	$P6_3/mmc$	Hexagonal
V_3S_4	1538235	C1 2/m 1	Monoclinic
V_2O_3	1537656	R-3c (:R)	Trigonal
VC	1011321	Fm-3m	Cubic
V	9012770	Im-3m	Cubic

The best fits of the coke data to structural models were obtained for hexagonal (P63/m) V_3S_4 (Fig. 7) and supplementary data file table x. Fitting was much improved by supposing only short range order (single scattering paths). This suggests that the V is highly dispersed, and does not form crystals with long range order in the coke.

Other possibilities considered for V in coke, included three other forms of sulfide, trigonal V_2O_3 and cubic VC. None of these gave give good fits.

The crystallographic structure for V_2S_3 is not available as a CIF file which raises the possibility that despite this named compound being sold by commercial chemical supplies and chosen here as a reference standard for XANES, the structure may not exist (although the alternative is simply that the structure has not been deposited in the databases). However, in view of the very good fit for the EXAFS with V_3S_4 and the poor fit of the XANES with "V_2S_3" it does not appear necessary to evaluate V_2S_3 in EXAFS.

The EXAFS analysis indicates the vanadium is bound as sulfide in the form of highly dispersed hexagonal P63/m V_3S_4, for all the cokes evaluated.
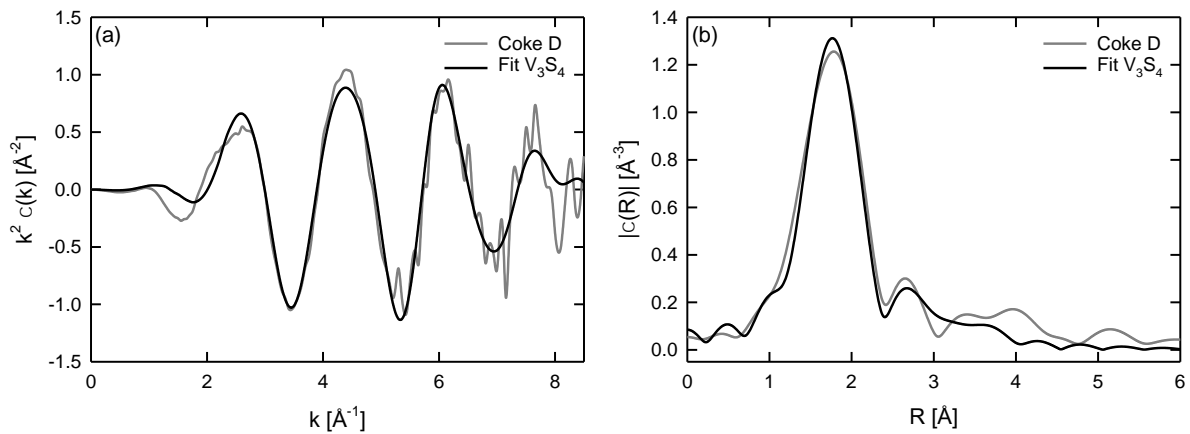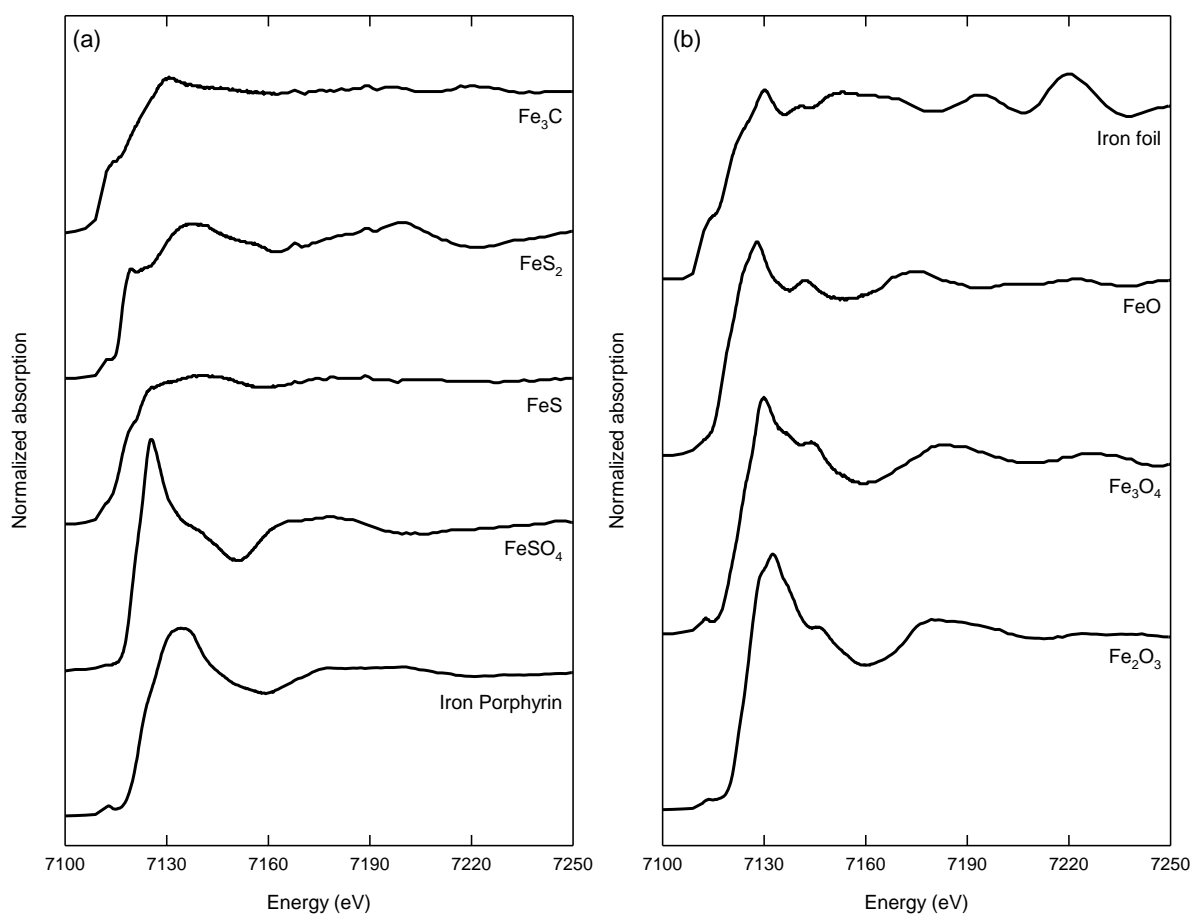
Figure 7. The experimental EXAFS spectrum for coke D and the FEFF theoretical fit for V_3S_4 hexagonal (P6$_3$/m) fitted for k from 2 to 8.5 Å^{-1} in (a) k^2-space and (b) R-space. R-factor = 0.045, S_0^2 = 0.505, ΔE_0 = -3.61 for most paths <4.6 Å.

3.5 Iron XANES

The reference compounds for Fe XANES display significant differences in the shape although not a large change in the edge position (Fig. 8).

Figure 8. The normalized absorption F K-edge XANES spectra for the reference compounds.

The Fe K-edge XANES of all five cokes appear similar. The coke E spectrum is presented here because it has the highest level of Fe of the anisotropic cokes and therefore the best signal to noise in these spectra (other data is available in the Supplementary data file).

All the cokes show similar Fe K-edge XANES spectra. The sulfides, FeS and FeS_2, are relatively good matches to the coke (Fig. 9). Iron porphyrin has a small pre-edge and then a higher energy edge than the coke spectra, so does not match the coke Fe K-edge spectra well. However, a small portion of iron porphyrin could shift the edge slightly and perhaps account for some of the differences between the spectra.
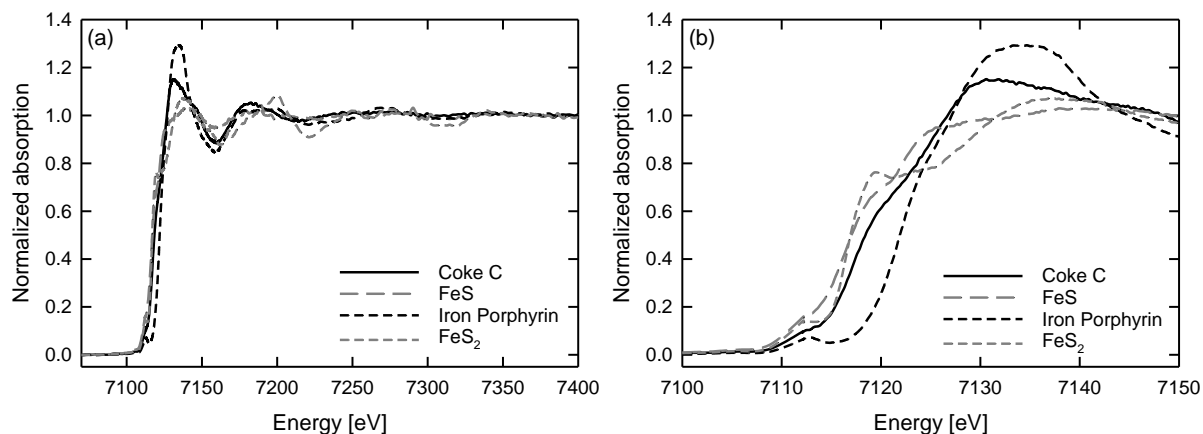
Figure 9. The normalized absorption iron K-edge XAS spectra for industrial coke C with reference spectra iron porphyrin, FeS_2 and FeS. (a) Whole energy region; (b) edge region.

The LCF provides estimates of the relative proportion of FeS, FeS_2 and iron porphyrin in the cokes (Supplementary data file Table x). The ratio of FeS and FeS_2 varies between the cokes with approximately one third or less of the Fe as organic iron porphyrin. Using only one of the sulfides and porphyrin in the fitting yields approximately the same results for the fraction of porphyrin vs. total sulfides. Using the normalized derivative spectrum gives a little bit less porphyrin and FeS, with an increase in FeS_2 for all cokes. The results thus show most iron in the cokes is bound as sulfides but with perhaps some proportion as an iron porphyrin.
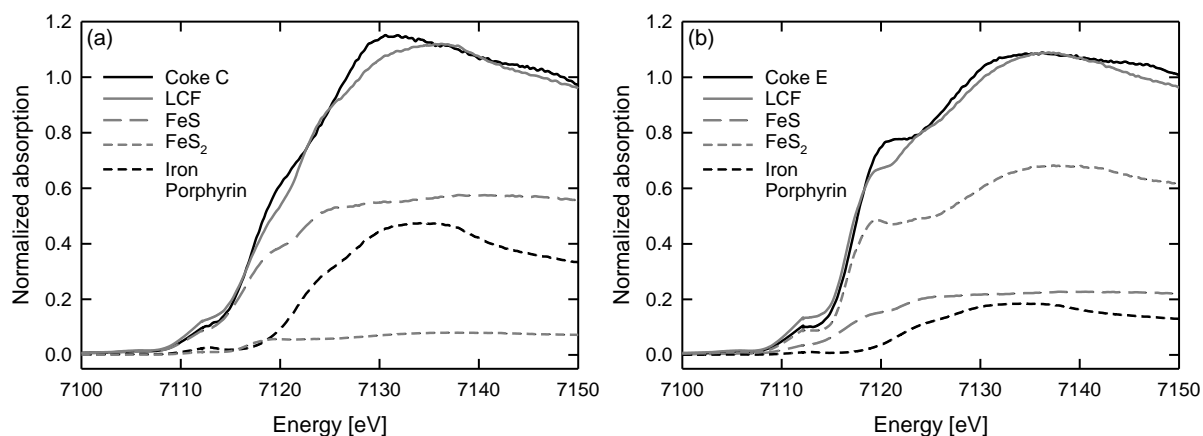
Figure 10. The linear combination fitting of the normalized absorption iron K-edge XANES spectra with nickel porphyrin, FeS_2 and FeS to (a) coke C and (b) coke E.

3.6 Iron EXAFS

For modelling of the EXAFS region, the spectra from the low iron cokes A, B and D are not of good enough quality for analysis. Therefore EXAFS modelling was only performed on cokes C, E and F. A variety of crystal structures (Table 5) were modelled and fitted to the spectra for the cokes. Of these only the iron sulfide compounds, FeS and FeS_2, gave reasonable fits (Supplementary Information Table x).

Table 5. Crystal structures tested for fit to the EXAFS of the cokes.

Compound	COD ID	Space group	Crystal system
FeS	1009043	P-62c	Hexagonal
FeS_2	1011013	Pnnm	Orthorhombic
FeS_2	1544891	Pa-3	Cubic
FeO	1011198	Fm-3m	Cubic
Fe_3C	1008725	Pnma	Orthorhombic
Fe		Im-3m	Cubic

The best fits (low R-factor, S_0^2 close to 1, ΔE_0 <5, good shape match) were obtained for hexagonal (P-62c) FeS (Fig. 11) but reasonable fits were also obtained for orthorhombic (Pnnm) FeS_2. Fitting was much improved by supposing only short range order. This suggests that the Fe is highly dispersed, and does not form crystals with long range order in the coke.

Other possibilities considered for Fe in coke, including FeO, Fe_3C did not give good fits, with either unrealistic S_0^2 values, large ΔE_0 (> 5) or poor (high) R-factors.
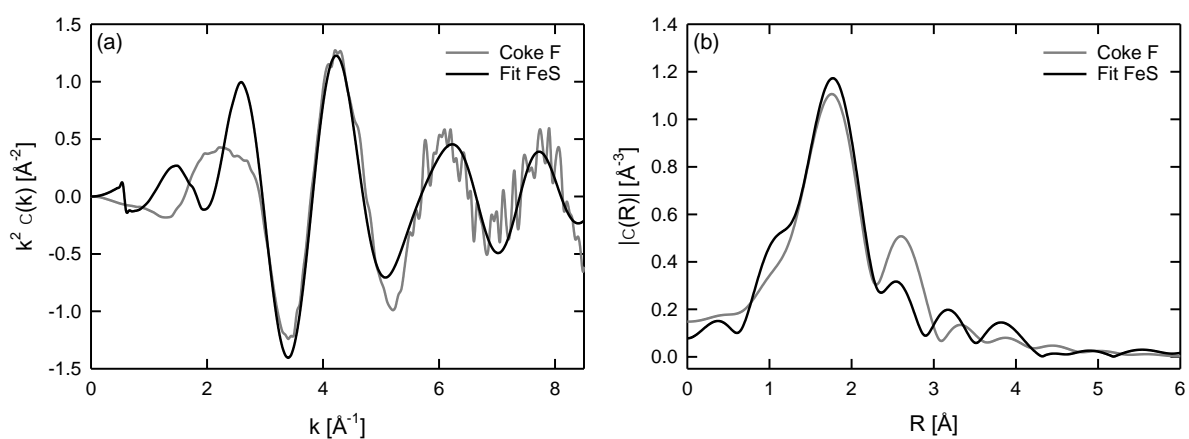
Figure 11. The experimental EXAFS spectrum for coke F and the FEFF theoretical fit for FeS hexagonal (P-62c) fitted for k from 3 to 8.5 $Å^{-1}$ in (a) k^2-space and (b) R-space. R-factor = 0.052, S_0^2 = 1.05, ΔE_0 = 1.25 for most paths <3 Å.

So in summary, the Fe XANES suggested FeS_2 and FeS with some Fe porphyrin, while EXAFS analysis indicates the cokes contain a sulfide with a structure similar to FeS hexagonal P-62c with short range order.

3.7 Metal species in petroleum coke

A good knowledge of the metal species present in the coke is provided by these XANES and EXAFS analyses. Each of the three elements studied V, Ni and Fe is present mainly as a

sulfide (where just a single structure was fitted). The sulfides are all hexagonally structured: NiS is primitive hexagonal P63/mmc, V_3S_4 is hexagonal P63/m and FeS is hexagonal P-62c. In each case there is only short range order. Short range order means one of two things - either the compound is highly disordered with no long range ordered crystal or molecular structure, or the compound is highly dispersed within the coke matrix.

There were no major differences in the chemistry of V, Ni and Fe between the six cokes studied.

3.8 Origin and development of the metal chemistry in coke

The metals V and Ni in coke are derived from crude oil. In crude oil these elements are found as soluble organometallic complexes, dominated by porphyrins where the metal is coordinated to N [17-19] and also non-porphyrin organic complexes where the metal is coordinated to S or O [20] [21]. The V is mostly as porphyrins in the more widely studied maltene (light) fraction of crude oil, but it is also present in porphyrins in the asphaltene (heavier) fraction [19]. Quite a wide range of V porphyrins exist in crude[25]. It is believed that the porphyrin complexes are derived from chlorophyll in the plant matter from which these deposits are derived (a Mg containing porphyrin) of heme from animal matter (a Fe containing porphyrin). The Mg is then exchanged with V and Ni during formation of the crude oil. We found an absence of work on Fe containing porphyrins in crude oil, which is perhaps surprising if heme could be one of the precursor molecules. On processing of crude oil, the metals concentrate in the heavy fractions and thus end up in the coke by-product rather than the light fractions.

The chemistry of V and Ni has been studied in petroleum cracking residues and petroleum cokes produced at low temperatures. Initially much of the Ni and V in Mayan residuum asphaltene is found (by XAS) to be present as porphyrins. However, after cracking at 425 °C

and 150 bar the residue contains only 10% of the Ni and V as porphyrins with the remainder in octahedral coordination [26]. Therefore, at these temperatures Ni and V porphyrins decompose and are converted to other forms. However, in petroleum cokes produced from oil sands such as the Athabasca Oil Sands of northern Alberta, Canada where Petroleum coke is produced during upgrading of oil sands bitumen to synthetic crude oil and the coke has high S and high metal content [27] much of the Ni and V (studied with XANES) remains as porphyrins [28]. These oil sand cokes are produced at lower temperatures (ca. 500 °C) than the cokes in the study presented here (1200-1250 °C) so these are not inconsistent, suggesting that the porphyrins are relatively stable at the lower temperature but are converted to sulfides at the temperatures typically used to produce coke suitable for anode production.

The Fe in the coke samples studied here appears to have converted from the unknown form it was found in the oil to FeS. Fe possibly started as porphyrins (this was not investigated) however, in the lower temperature treated oil sand cokes Fe has been found (with XANES) to be present as thiophenic coordination and pyritic-ilmenitic (FeS_2-$FeTiO_3$) coordination [29]. In high sulfur petroleum coke from a refinery, prepared at 950-1100 °C, Fe was found mostly in the form of Fe_3C (using XRD) but on CO_2 gasification some Fe reacts with S to form FeS, while some is reduced to Fe^0 and some is oxidised to FeO, Fe_2O_3, and Fe_3O_4 [30]. Therefore the FeS found in the petroleum cokes studied here, considering the conditions of formation of the coke, is consistent with these other studies.

The metal sulfides have formed within a carbon matrix. The EXAFS work here found the metal sulfides are all hexagonally structured (although there are many sulfides known that do not have hexagonal structures) with only short range order. The graphite matrix in which these sulfides form has a hexagonal P 63mc structure. Therefore it could be supposed that the graphite may have acted as a template in the formation of these sulfides during heating to form coke. Considering the origin of these compounds, derived from species soluble in the

organic phase, where the metals start out highly dispersed, it seems likely that they remain highly dispersed when the coke is formed with limited ability to coalesce, rather than simply amorphous. Therefore the metal sulfides are likely not present as inclusions. Mapping of oil sands cokes show a broad and fairly uniform distribution of V and Ni with only slight concentration at the surfaces of the coke particles, supporting this supposition [28].

3.9 Sulfur chemistry in cokes

The S in cokes is only partially tied up in the metal sulfides. V, Ni and Fe sulfides in these cokes only accounts for ca. 1% of the total sulfur in the coke. The dominant form of the S in coke is not sulfide, but appears to be organic or S–S bound sulfur [16].

3.10 Metal sulfides and anode reactivity

It has previously been established that the presence of particular metals in anodes affects the reactivity. Vanadium has been shown to be an active catalyst for the carboxy reactivity of anodes at elevated temperatures[3, 4] and air reactivity[31]. Nickel has been shown to have a negative effect on both air burn and carboxy reactivity[4, 5]. Fe is also an active catalyst for airburn and the CO_2 reaction[7] to the extent that is can been seen as beneficial in petroleum coke beneficial for the related CO_2 gasification catalytic reactions [32]. In the work presented here, we have shown that the metals are present as sulfides of V, Ni and Fe. So now there is the possibility to investigate how these particular metal species act to drive theair burn and carboxy reactions. While correlations have been established between the air reactivity or the carboxy reactivity and the V, Ni or Fe content (including with these cokes[33]) the detailed mechanisms of the reactions involving the metal compounds have not been established. If knowledge of the reaction mechanisms could be investigated, now that

we know the identity of the metal compounds present in these materials, it may be possible to poison these metal sulfide "catalysts" to mitigate the negative effect of high metal impurity levels.
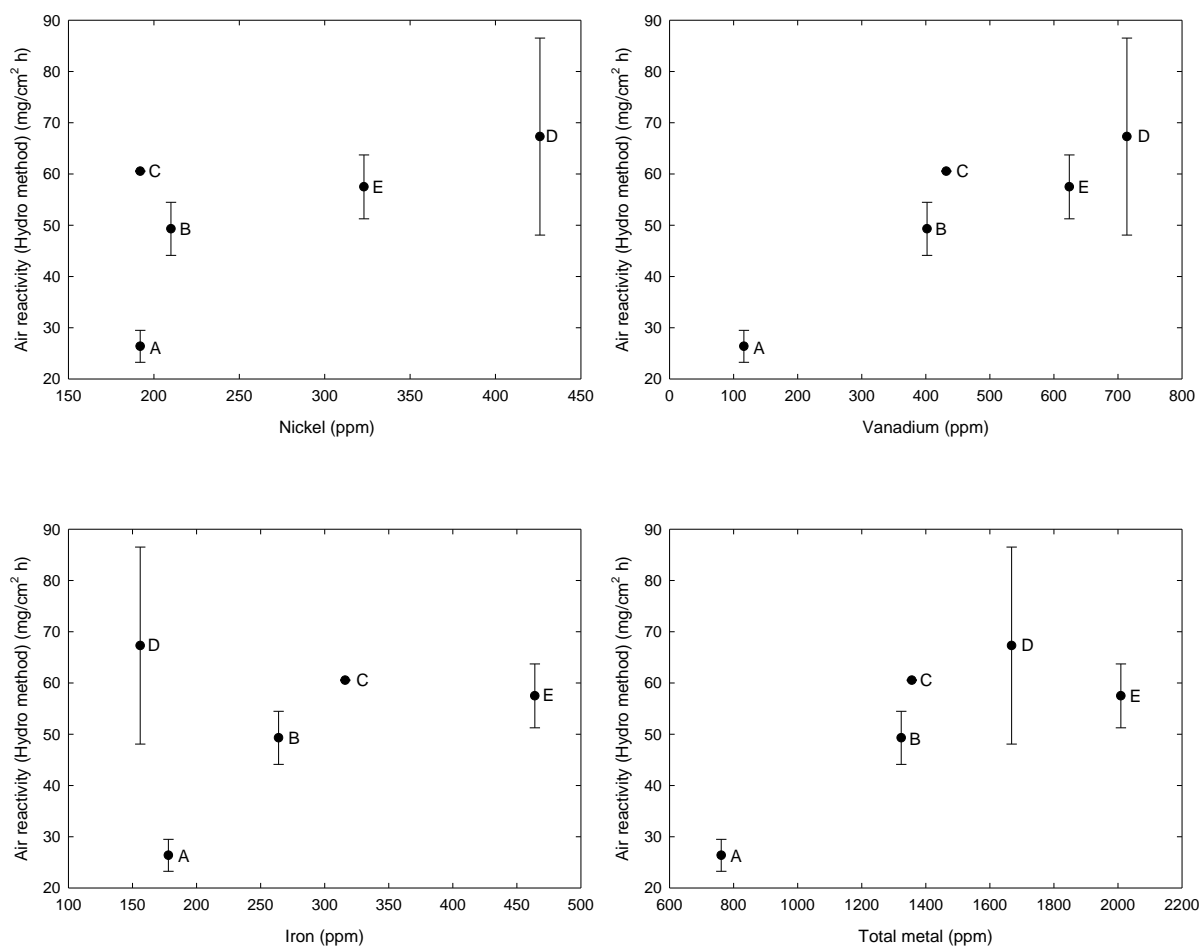
Figure 12. Air reactivity vs. the different metals for anodes made by the different cokes.

4. Conclusions

It has been shown that for high sulfur cokes containing high levels of V, Ni and Fe, the metals are present as hexagonal sulfides. The metals are very highly dispersed through the carbon matrix, and are not present as crystalline inclusions. These sulfides arise from reactions occurring at the high temperatures involved in coking, and are derived from the soluble metal porphyrins and other organic complexes in the heavy oil fractions. Only a small

portion of the S present in the coke is bound as metal sulfides, with the bulk of the sulfur is present as S-S bonded sulfur. The presence of the V, Ni and Fe affects the airburn and CO_2 reactivity, acting as a catalyst for these reaction. Although this study has not investigated the mechanism by which the catalysis occurs, this new knowledge of the chemical species present will enable an informed study into the catalysis reactions.

Acknowledgements

References

[1] J. Thonstad, P. Fellner, G.M. Haarberg, J. Híveš, H. Kvande, Å. Sterten, Aluminium electrolysis : fundamentals of the Hall-Héroult process, 3rd ed. ed., Aluminium-Verlag, Düsseldorf, 2001.

[2] L. Edwards, The History and Future Challenges of Calcined Petroleum Coke Production and Use in Aluminum Smelting, JOM, 67 (2015) 308-321.

[3] G.J. Houston, H.A. Øye, Consumption of anode carbon during aluminium electrolysis, Aluminium-Verlag, Düsseldorf, 1985.

[4] T. Eidet, J. Thonstad, Effects of sulphur, nickel and vanadium on the air and CO_2 reactivity of cokes, s.n., S.l., 1997.

[5] Z. Li, N. Zhang, L. Wen, Effect of Nickel Content on Carbon Anode Reactivity, Asian J. Chem., 28 (2016) 1703-1707.

[6] L. Edwards, Impurity level distribution in GPC and CPC and impact on anode properties, Light Met., 2014 (2014) 1093-.

[7] T. Eidet, J. Thonstad, M. Sørlie, Effects of iron and sulphur on the air and CO_2 reactivity of cokes, Light Met., (1997) 511-517.

[8] J.d.S. Batista, B.I.d. Silveira, Influence of the sodium content on the reactivity of carbon anodes, Materials Research, 11 (2008) 387-390.

[9] S.M. Hume, W.K. Fischer, R.C. Perruchoud, J.B. Metson, J.B. Baker, Influence of Petroleum Coke Sulphur Content on the Sodium Sensitivity of Carbon Anodes, Light Met., (1993) 535-541.

[10] Y.D. Bensah, T. Foosnaes, The nature and effect of sulphur compounds on co 2 and air reactivity of petrol coke, J. Eng. Appl. Sci., 5 (2010) 35-43.

[11] M. Sørlie, Effect of sulphur on anode reactivity and electrolytic consumption, Light Met., (1994) 659−665.

[12] S.J. Hay, J. Metson, M.M. Hyland, Sulfur speciation in aluminum smelting anodes, Ind. Eng. Chem. Res., 43 (2004) 1690-1700.

[13] J. Xiao, Q. Zhong, F. Li, J. Huang, Y. Zhang, B. Wang, Modeling the change of green coke to calcined coke using Qingdao high-sulfur petroleum coke, Energy and Fuels, 29 (2015) 3345-3352.

[14] Q. Zhong, J. Xiao, H. Du, Z. Yao, Thiophenic Sulfur Transformation in a Carbon Anode during the Aluminum Electrolysis Process, Energy and Fuels, 31 (2017) 4539-4547.

[15] J. Xiao, S.-y. Deng, Q.-f. Zhong, S.-l. Ye, Effect of sulfur impurity on coke reactivity and its mechanism, T. Nonferr. Metal. Soc., 24 (2014) 3702-3709.

[16] G. Jahrsengene, H.C. Wells, S. Rørvik, A.P. Ratvik, R.G. Haverkamp, A.M. Svensson, A XANES Study of Sulfur Speciation and Reactivity in Cokes for Anodes Used in Aluminum Production, Metall. Mater. Trans. B, 49B (2018) 1434-1443.

[17] G. Caumette, C.P. Lienemann, I. Merdrignac, B. Bouyssiere, R. Lobinski, Element speciation analysis of petroleum and related materials, J. Anal. Atom. Spectrom., 24 (2009) 263-276.

[18] J. Goulon, A. Retournard, P. Friant, C. Goulon-Ginet, C. Berthe, J. Muller, J. Poncet, R. Guilard, J. Escalier, B. Neff, Structural characterization by X-ray absorption spectroscopy (EXAFS/XANES) of the vanadium chemical environment in Boscan asphaltenes, J. Chem. Soc. Dalton, (1984) 1095-1103.

[19] G.P. Dechaine, M.R. Gray, Chemistry and association of vanadium compounds in heavy oil and bitumen, and implications for their selective removal, Energ. Fuel, 24 (2010) 2795-2808.

[20] J.G. Reynolds, E.J. Gallegos, R.H. Fish, J.J. Komlenic, Characterization of the Binding Sites of Vanadium Compounds in Heavy Crude Petroleum Extracts by Electron Paramagnetic Resonance Spectroscopy, Energ. Fuel, 1 (1987) 36-44.

[21] J.G. Reynolds, W.R. Biggs, Application of Size Exclusion Chromatography Coupled with Element-Specific Detection to the Study of Heavy Crude Oil and Residua Processing, Acc. Chem. Res., 21 (1988) 319-326.

[22] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Rad., 12 (2005) 537-541.

[23] S. Graulis, D. Chateigner, R.T. Downs, A.F.T. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeck, A. Le Bail, Crystallography Open Database - An open-access collection of crystal structures, J. Appl. Crystallogr., 42 (2009) 726-729.

[24] G. Jahrsengene, H.C. Wells, C. Sommerseth, A.P. Ratvik, L.P. Lossius, R.G. Haverkamp, A.M. Svensson, Vanadium Speciation in Petroleum Cokes for Anodes used in Aluminium Electrolysis in: Proceedings of 35th International ICSOBA Conference, Hamburg, Germany, 2 – 5 October, 2017, 2017, pp. 617-624.

[25] B.M. Rytting, I.D. Singh, P.K. Kilpatrick, M.R. Harper, A.S. Mennito, Y. Zhang, Ultrahigh-Purity Vanadyl Petroporphyrins, Energ. Fuel, 32 (2018) 5711-5724.

[26] J.T. Miller, R.B. Fisher, Structural determination by XAFS spectroscopy of non-porphyrin nickel and vanadium in Maya residuum, hydrocracked residuum, and toluene-insoluble solid, Energ. Fuel, 13 (1999) 719-727.

[27] J.A. Nesbitt, M.B.J. Lindsay, Vanadium Geochemistry of Oil Sands Fluid Petroleum Coke, Environ. Sci. Technol., 51 (2017) 3102-3109.

[28] J.A. Nesbitt, J.M. Robertson, L.A. Swerhone, M.B.J. Lindsay, Nickel geochemistry of oil sands fluid petroleum coke deposits, Alberta, Canada, FACETS, 3 (2018) 469-486.

[29] J.A. Nesbitt, M.B.J. Lindsay, N. Chen, Geochemical characteristics of oil sands fluid petroleum coke, Appl. Geochem., 76 (2017) 148-158.

[30] Z.J. Zhou, Q.J. Hu, X. Liu, G.S. Yu, F.C. Wang, Effect of iron species and calcium hydroxide on high-sulfur petroleum coke CO_2 gasification, Energ. Fuel, 26 (2012) 1489-1495.

[31] J.G. Rolle, Y.K. Hoang, Studies of the Impact of Vanadium and Sodium on the Air Reactivity of Coke and Anodes, Light Met., 1995 (1995).

[32] L. Ren, R. Wei, Y. Gao, Co-gasification reactivity of petcoke and coal at high temperature, Fuel, 190 (2017) 245-252.

[33] G. Jahrsengene, S. Rørvik, A.P. Ratvik, L.P. Lossius, R.G. Haverkamp, A.M. Svensson, Reactivity of Coke in Relation to Sulfur Level and Microstructure" TMS, 10-14 March 2019, San Antonio, TX, USA in: TMS, 1-14 March, San Antonio, TX, USA 2019.