

A XANES Study of Sulfur Speciation and Reactivity in Cokes for Anodes Used in Aluminum Production



GØRIL JAHRSENGENE, HANNAH C. WELLS, STEIN RØRVIK,
ARNE PETTER RATVIK, RICHARD G. HAVERKAMP, and ANN MARI SVENSSON

Availability of anode raw materials in the growing aluminum industry results in a wider range of petroleum cokes being used to produce carbon anodes. The boundary between anode grade cokes and what previously was considered non-anode grades are no longer as distinct as before, leading to introduction of cokes with higher sulfur and higher trace metal impurity content in anode manufacturing. In this work, the chemical nature of sulfur in five industrial cokes, ranging from 1.42 to 5.54 wt pct S, was investigated with K-edge XANES, while the reactivity of the cokes towards CO₂ was measured by a standard mass loss test. XANES identified most of the sulfur as organic sulfur compounds. In addition, a significant amount is identified (16 to 53 pct) as S-S bound sulfur. A strong inverse correlation is observed between CO₂-reactivity and S-S bound sulfur in the cokes, indicating that the reduction in reactivity is more dependent on the amount of this type of sulfur compound rather than the total amount of sulfur or the amount of organic sulfur.

<https://doi.org/10.1007/s11663-018-1215-x>
© The Author(s) 2018

I. INTRODUCTION

HIGH-QUALITY carbon anodes are critical to the economy of aluminum production. Anode carbon, which is consumed during electrolysis, makes up around 11 to 13 pct of the cost of aluminum production.^[1] Anodes are produced by mixing calcined petroleum coke, recycled anode butts, and coal tar pitch before being subject to a baking cycle up to 1200 °C. Smelters require anodes with high-density, low-impurity levels (*e.g.*, V, Ni, Fe, Si, Na, Ca, Mg, and Al), and low thermal expansion to achieve predictable performance in the cells, usually achieved by blending different cokes. Sulfur is usually specified around 1.5 to 2 wt pct based on operational experience, and in some cases restricted due to limitations on SO₂ to the atmosphere for smelters without SO₂ scrubbing.

The availability of high-quality anode grade calcined petroleum cokes for use in anodes is declining, resulting in challenges for the aluminum industry. One reason for

the reduction in coke quality is that sour crude oils, with high sulfur and other impurity content and higher specific gravity, are now favored by many refineries because they are more available and of lower cost than the lightweight, low sulfur, sweet oils.^[2] Petroleum coke is produced from the heavy residual fractions of crude oil, the fraction that tends to be highly concentrated in impurities (including sulfur), and with improved techniques for extracting the volatile fractions the quality of the coke decreases. This results in cokes with higher sulfur content, usually accompanied by an increase in metal trace impurities. An almost linear relationship between sulfur and vanadium content is observed in most cokes,^[3] although the relationships tend to be more scattered for cokes very high in vanadium or sulfur. Vanadium promote carbon reactivity with air, resulting in an increase in anode consumption if the anode cover material is not completely sealing the top and sides of the anode.^[4]

It is important to understand that there is not a shortage of coke, it is only the availability of good anode-grade cokes that are not covering the demand of the aluminum industry. Hence, the smelters have to learn to cope with this gradual decline in availability of high-quality raw materials. Because of the limited availability of high-quality cokes, the use of shot coke, previously described as fuel grade, has been investigated as one alternative.^[2,5]

Sulfur is present in cokes in a variety of forms. In crude oil, more than 1500 sulfur compounds have been identified.^[6] During calcination of green coke and

GØRIL JAHRSENGENE and ANN MARI SVENSSON are with the NTNU Norwegian University of Science and Technology, 7491 Trondheim, Norway. Contact e-mail: annmari.svensson@ntnu.no
HANNAH C. WELLS and RICHARD G. HAVERKAMP are with the Massey University, Palmerston North 4222, New Zealand. STEIN RØRVIK and ARNE PETTER RATVIK are with the SINTEF Industry, 7465 Trondheim, Norway.

Manuscript submitted September 22, 2017.

Article published online March 26, 2018.

baking of the anode, thermal processes may change the chemical form of sulfur. Sulfur can be present as a part of the carbon lattice, attached to side chains, between aromatic sheets, on the surface of clustered molecules or on surfaces and pores bound by capillary condensation, adsorption, or chemisorption.^[7]

XANES (X-ray absorption near-edge structure) spectroscopy is a powerful technique when analyzing sulfur chemistry in solids. It has been used to investigate organic and inorganic sulfur bonding in coals,^[8,9] varying heavy petroleum,^[10] materials for electrodes in batteries,^[11] as well as in different earth materials and sediments.^[12–14] In a selection of industrial anode cokes and baked anodes, XANES revealed the sulfur speciation to be organic sulfur rings, primarily as thiophene-containing polycyclic aromatic hydrocarbons.^[15] Thiophenes have also been detected in cokes by a combination of X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and simulations.^[16] How these sulfur-containing hydrocarbons transform during electrolysis, mainly by producing COS and SO₂ gases, has also been investigated.^[15,17]

For non-electrochemical (secondary) reactions such as air burn, CO₂ burn, and carbon dusting, cell temperature, anode manufacturing parameters, and raw material properties (coke and pitch) are important. Specific metal impurities in the coke, *e.g.*, vanadium, are known to catalyze reactions between carbon and oxygen, and carbon and produced CO₂, increasing the carbon consumption.^[18] The reaction between carbon and air is not believed to be significantly affected by sulfur,^[19] and the increase usually observed with higher sulfur cokes is believed to be caused by the parallel increase in metal catalyst content, while sulfur is believed to have a positive effect on the reaction between carbon and produced CO₂.^[20–24] Sulfur may have a negative effect on the total carbon consumption due to electrochemically produced COS.^[25] Increasing sulfur while holding metal content constant revealed an increase for both air and CO₂ reactivity.^[26] The actual effect should be investigated in combination with metal impurities, as it is believed that the decrease in CO₂ reactivity may be due to the formation of inactive metal-sulfur complexes during carbonization.^[27] Sulfur also depresses the catalytic effect of sodium, which enters the anodes through butts, perhaps as a Na-S-O complex.^[28] Most investigations have, however, been done through doping, for example, for vanadium, nickel, iron, and sulfur,^[29,30] and does not necessarily reflect the actual coke conditions if the impurities are not in the same chemical state or form as in the industrially produced coke.

In this study, the CO₂ reactivity and sulfur speciation of industrial cokes with varying levels of sulfur, metallic impurities, and isotropy, are measured. By choosing industrial cokes with varied composition, rather than chemically doped cokes, a realistic assessment of chemical speciation and the relationships between composition and reactivity is sought.

II. EXPERIMENTAL SECTION

A. Coke

Five calcined petroleum cokes (designated A-E) originating from different crude oils produced by different industrial manufacturers were selected from a larger group of cokes based on vanadium and sulfur content. The cokes are calcined at 1200 to 1250 °E, where °E is an equivalent temperature representing the baking level, a method frequently used by the industry.^[31] This method is based on assessment of changes in crystallinity, *i.e.*, L_c , of a calibrated reference coke sample inserted in the furnace.

B. Elemental Analysis and CO₂ Reactivity

Coke impurities were determined by X-ray fluorescence (XRF) according to ISO 12980:2000 on the bulk coke materials (single source coke), from which the contents of both metallic impurities and sulfur were identified. The CO₂ reactivity was determined using a standard mass loss test (RDC Equipment) for coke CO₂ reactivity according to ISO-12981-1 Standard RDC-1141, where the mass loss of 5 g coke with grain size 1 to 1.4 mm is determined after being exposed to a CO₂ gas flow rate of 50 L/h for 100 minutes at 1000 °C.

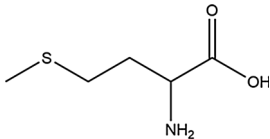
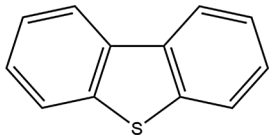
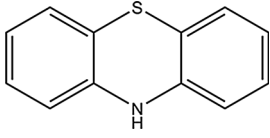
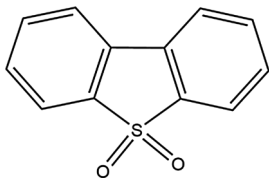
C. Isotropy

Optical texture was characterized by studying epoxy-mounted and polished coke samples under polarized light using a Leica/Reichert MeF3A metallurgical optical reflected light microscope. For each coke, 144 grains of ~0.75 mm size were captured at ×250 optical magnification. A macro running within NIH Image Software was employed to determine the fiber and mosaic indexes of the cokes.^[32] The degree of isotropy is determined by the mosaic index, a parameter describing the fineness of the optical domains, while the degree of anisotropy is determined by the fiber index which describes the degree of alignment of the optical domains.

D. XANES

Sulfur K-edge XANES was performed at the Canadian Light Source (CLS) in Saskatoon, Canada on the soft X-ray microcharacterization beamline (SXRMB) 06B1-1. This provides a resolution ($\Delta E/E$) of 1×10^{-4} and a flux of around 1×10^{11} photons s⁻¹. Coke and reference samples were analyzed as ground powder. The reference compounds were chosen based on previous work^[15] to represent a range of aromatic organic sulfur compounds containing different functional groups that could approximate the functionalized amorphous and graphitic carbon of the cokes, and inorganic compounds that represent a range of oxidation states of sulfur associated with known impurity elements in cokes (Table I). XAS was recorded from 2452 to 2532 eV with a step size of 2 eV pre-edge, 0.10 eV over the edge region, and 0.75 eV post edge, all with a dwell time of 1 second. Spectra were collected in both fluorescence

Table I. Reference Compounds Used in S K-edge XANES

Name	Composition/Structure
Inorganic S	
Elemental sulfur/graphite	25 pct S
Sodium sulfate	Na ₂ SO ₄
Sodium metabisulfite	Na ₂ S ₂ O ₅
Sodium sulfite	Na ₂ SO ₃
Potassium sulfate	K ₂ SO ₄
Potassium thiosulfate	K ₂ S ₂ O ₃
Potassium thiocyanate	KSCN
Iron(II)sulfide	FeS
Organic S	
L-methionine	 <chem>CH3SCH2CH2CH(NH2)CO2H</chem>
Dibenzothiophene	 <chem>C12H8S</chem>
Phenothiazine	 <chem>C12H9NS</chem>
Dibenzothiophene sulfone	 <chem>C12H8O2S</chem>

yield mode (FLY) and total electron yield mode (TEY). Three scans of each sample were collected and afterwards combined.

The S XANES spectra of the cokes were fitted using Athena software^[33] with linear combinations of normalized $\mu(E)$ spectra of reference compounds with E_0 constrained for each component to the fitted value for that component (LCF). Athena uses non-linear least squares minimization for fitting. A 50 eV energy range was used for the fit (20 eV below E_0 to 30 eV above E_0). Initially, a combinatorial fit was performed using a wide range of standards, then this was refined to promising candidates for the final fit. Linear combination fits were also tested with derivative $\mu(E)$ and $\chi(k)$ and these gave very similar best fit combinations. The accuracy of this

technique depends on a sensible selection of standards, based on some knowledge of the possible chemistry, and the extent of the differences between the spectra of the standards used. In the compounds investigated here, the standards had spectra of substantially different shapes and this increases the confidence of the validity of the fit.

III. RESULTS

A. Elemental Composition

The composition of the cokes as measured by XRF varied in sulfur content in the range 1.42 to 5.54 wt pct, and vanadium between 116 and 714 ppm (Table II). The

Table II. Composition of the Five Cokes Measured by XRF

	S/Wt Pct	V/ppm	M/ppm
Coke A	1.42	116	761
Coke B	3.56	402	1323
Coke C	5.54	432	1356
Coke D	3.82	714	1668
Coke E	4.42	624	2009

M includes Na, Mg, Al, Si, Ca, V, Fe, and Ni.

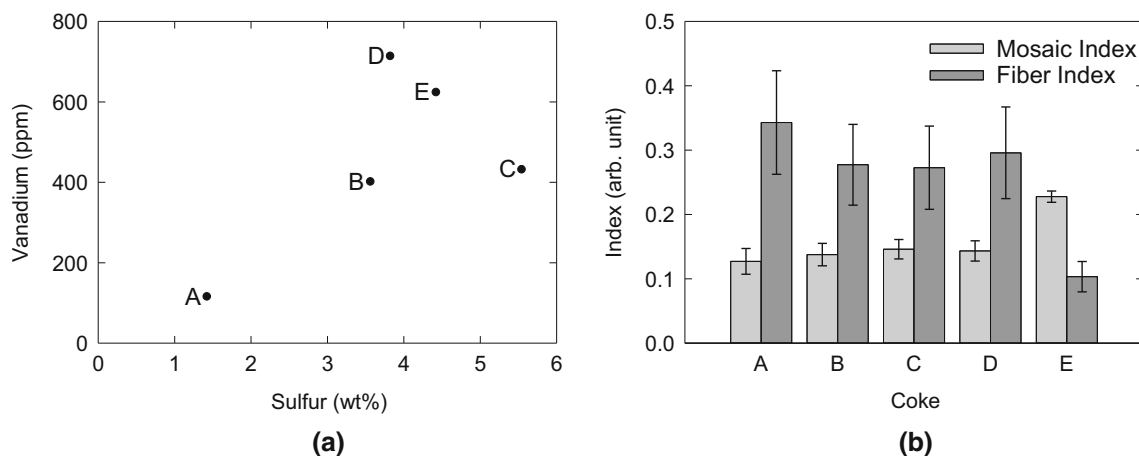


Fig. 1—(a) Level of vanadium vs level of sulfur for cokes A-E; (b) Mosaic and fiber index for cokes A-E.

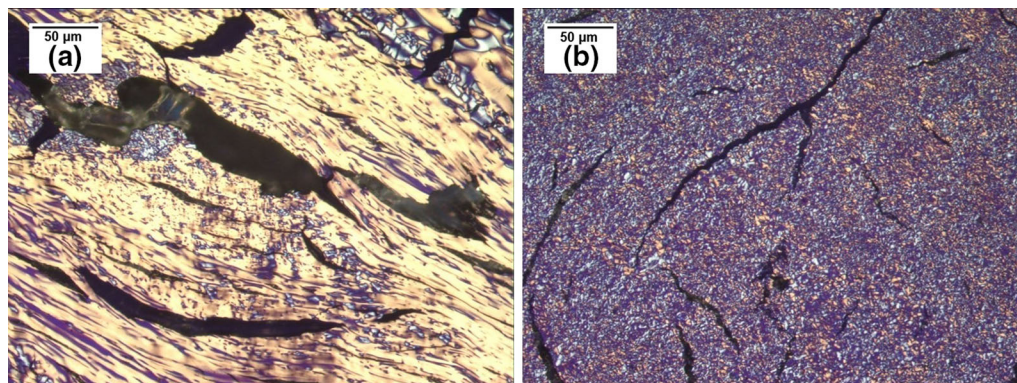


Fig. 2—Optical microscopy images of coke grains under polarized light. (a) Anisotropic structure of coke A; (b) Isotropic structure of coke E.

relationship between sulfur and vanadium concentration in the cokes is shown in Figure 1(a).

B. Isotropy

The four cokes A-D have similar mosaic and fiber indices and all are categorized as anisotropic (Figure 1(b)). Coke A is the most anisotropic of these. Coke E has a higher mosaic index and a lower fiber index than the other cokes indicating a more isotropic coke. In each of the cokes A-D, there was a relatively large variation in isotropy among the 144 grains investigated for each coke. This is reflected in the relatively high standard deviations of the mosaic and

fiber indices. A typical anisotropic structure identified within cokes A-D is shown in Figure 2(a). In Figure 2(b), a typical highly isotropic structure identified in all the grains of coke E is shown. In comparison, relatively few isotropic grains were identified in cokes A-D. The high standard deviations observed in the anisotropic cokes are due to the heterogeneous nature of coke as a material; by experience these cokes are similar to other commercially available cokes.

C. XANES

Although both TEY and FLY sulfur K-edge spectra were recorded, self-absorption was a problem at the

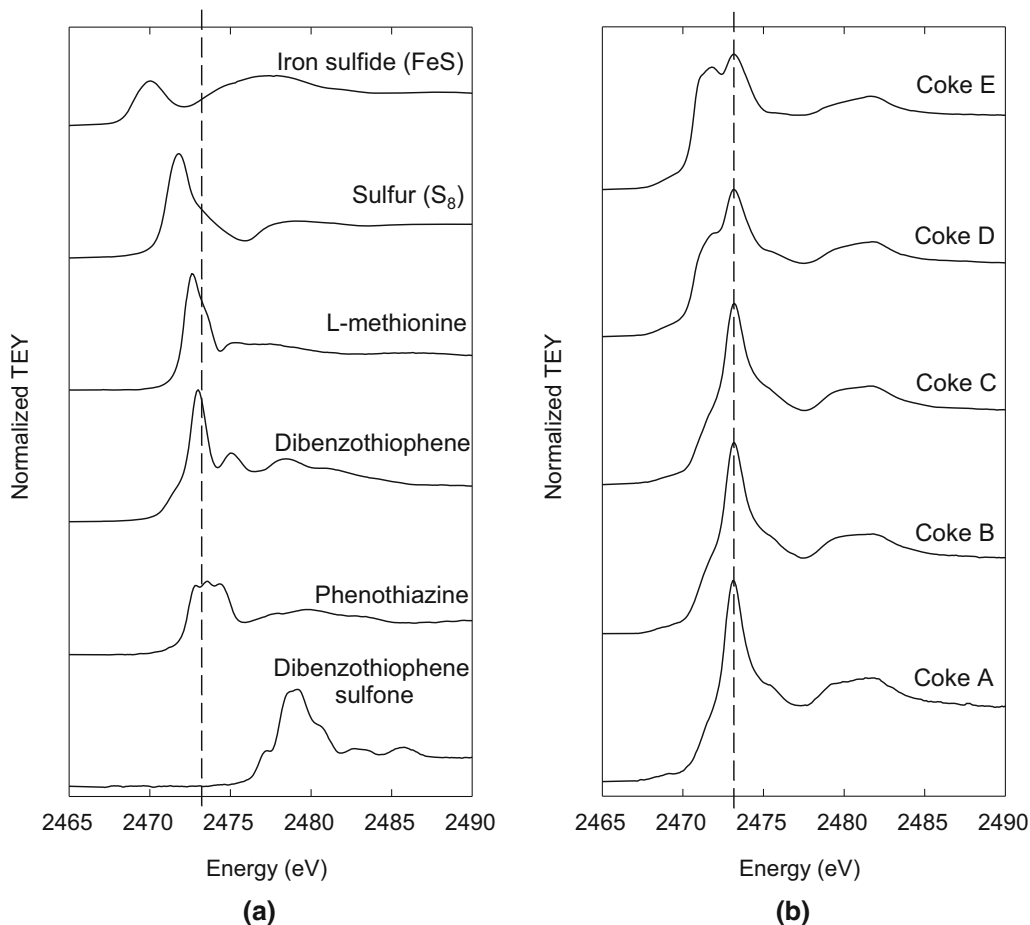


Fig. 3—Normalized (to step edge = 1) sulfur K-edge XANES for the (a) reference organic standards, sulfur (S_8) and iron(II)sulfide; (b) industrial cokes A-E. The vertical lines in both figures mark the main peak position in the coke spectra.

edge in many of the FLY spectra so only TEY spectra have been used in the analysis. Figures 3(a) and 4 show the resulting S XANES spectra for the reference compounds. The vertical line is the position of the main peak in the coke spectrum, presented in Figure 3(b). All the reference standards and the cokes were stable under the X-ray beam with the exception of dibenzothiophene which displayed significant changes to the spectra after each scan. Therefore, multiple scans were merged for all samples and standards except for dibenzothiophene. It was noted that phenothiazine gave a purple fluorescence under X-ray irradiation.

Some major differences were evident in the S K-edge XANES spectra of the cokes (Figure 3(b)). Cokes A, B, and C are very similar to each other. A slight broadening to the left of the main peak is observed in these cokes, and a small contribution of a sulfur species with a lower energy edge is evident. Coke D has a low-energy shoulder to the left of the main peak, evolving to a visible peak in coke E, indicating a much higher contribution of an additional sulfur compound with a low-energy peak in these two cokes than the other three.

An identification of the main components of the coke spectra was achieved by linear combination fitting

(LCF) with the reference spectra. A good fit was obtained for cokes A-C using two aromatic sulfur compounds, phenothiazine and dibenzothiophene, with a contribution of S_8 (Figure 5(a)). The main edge for S_8 is at lower energy than for most of the other standards (of higher nominal oxidation state) which provides some certainty in the fitting of this component to the cokes. Other options for this component are considered in the discussion. In cokes D and E, it is apparent that this low-energy component is present in a higher proportion, and the LCF fitting supports this by eliminating the main organic specie by using coke C as a component in the LCF (Figure 5(b)). The portion of identified S_8 ranges from 16 pct of the S in coke A to 53 pct of the S of coke E (Table III).

D. CO_2 Reactivity and Sulfur

The relationship between CO_2 reactivity and total sulfur content is given in Figure 7(a), showing an overall trend that low-sulfur cokes are more reactive than high-sulfur cokes, while among the high-sulfur cokes there is no direct relationship between reactivity and total sulfur content. Evaluating only the organic sulfur

in Figure 7(b), cokes D and E have very low reactivity and low organic sulfur content, indicating something other than this type of sulfur is lowering the reactivity. A stronger relationship is observed, however, when the CO₂ reactivity is plotted against the amount of sulfur identified as S₈ by LCF present in the cokes

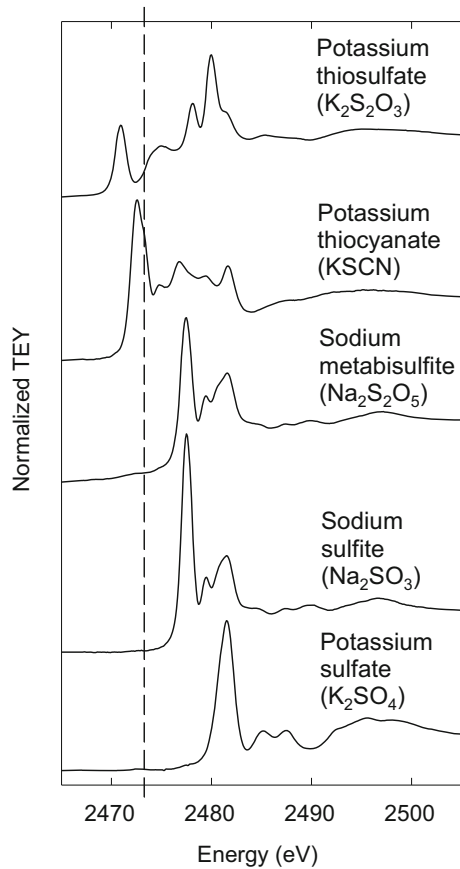
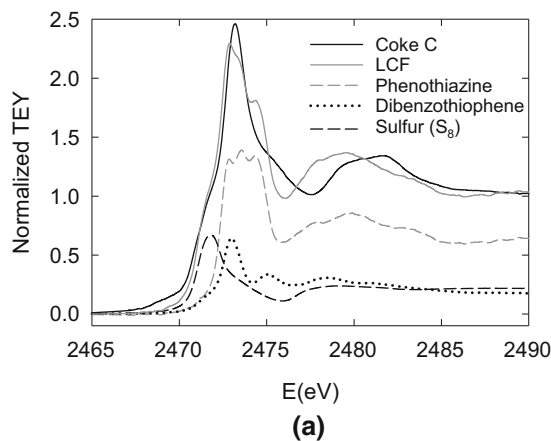


Fig. 4—Normalized (to step edge = 1) sulfur K-edge XANES for potassium thiosulfate, potassium thiocyanate, sodium metabisulfite, sodium sulfite, and potassium sulfate. The sodium sulfite and potassium sulfate are shrunk to 70 pct compared to the remaining spectra. The vertical line marks the main peak position in the coke spectra (Fig. 3(b)).



(Figure 7(c)). Last, the CO₂ reactivity vs ratio of sulfur/metal in Figure 7(d) indicates a difference between cokes D and E from the remaining cokes due to its very low reactivity compared to the ratio.

IV. DISCUSSION

The XANES analysis of the cokes has shown that sulfur is present as both organic sulfur and, apparently, as sulfur not bound in the aromatic structure (S₈). The LCFs in Figures 5 and 6 indicate that the low-energy peak of S₈ is causing the left shoulder in the coke spectra. However, this is not the only option; not included in this study is pyritic sulfur (oxidation state -1, MeS₂ where Me indicates a metal)^[15] and disulfides (oxidation state 0, R-S-S-R bonding)^[34,35] which both have the K-edge peak in the same area as S₈. These low-energy peaks are known to be caused by S-S bonding, and other compounds with S-S bonding all exhibit this feature (e.g., observed for potassium thiosulfate in Figure 4). Compounds with S-S bonding are therefore difficult to distinguish from each other using K-edge fingerprinting, and sulfur identified as S₈ will be referred to as S-S bound sulfur.

The presence of S-S bound sulfur was not observed in large quantities in a previous XANES study of cokes,^[15,36] but has previously been suggested based on XPS measurements.^[16] The proportions of S-S bound sulfur (identified from S₈ in the LCF) vary between the different cokes from 16 to 53 pct of the total S giving 0.3 to 2.3 wt pct of this kind of sulfur in the cokes. The exact kind of compound is unknown, but large amounts of sulfides with sulfur in the oxidation state -1 (e.g., FeS₂) are unlikely due to the much higher quantity of sulfur vs metals (Figure 7(d)). Metal sulfides with a lower oxidation number of -2 (e.g., FeS) are not observed. If all metal impurities in coke E (2009 ppm, 0.06 mole pct) is bound as MeS₂, only 0.12 mole pct of the total 1.7 mole pct S would be bound this way. This is only 7 pct of the total sulfur in the coke, and much less than the S₈ fitted contribution of 53 pct, indicating that the contribution from metal sulfides can only be

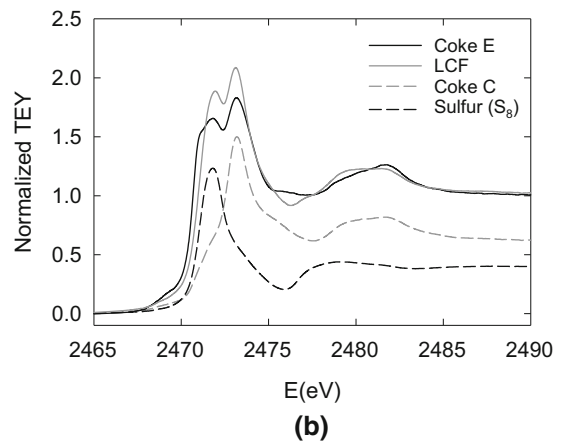


Fig. 5—K-edge XANES spectra of (a) coke C fitted with two organic references and sulfur (S₈); (b) coke E fitted with coke C and sulfur (S₈).

Table III. Relative Amounts of Sulfur Contained in Different Compounds Estimated from the Linear Combination Fitting (LCF) of the Five Cokes

	Phenothiazine	Dibenzothiophene	Sulfur (S_8)
Coke A	0.60	0.24	0.16
Coke B	0.60	0.20	0.20
Coke C	0.63	0.16	0.21
Coke D	0.53	0.06	0.41
Coke E	0.44	0.03	0.53

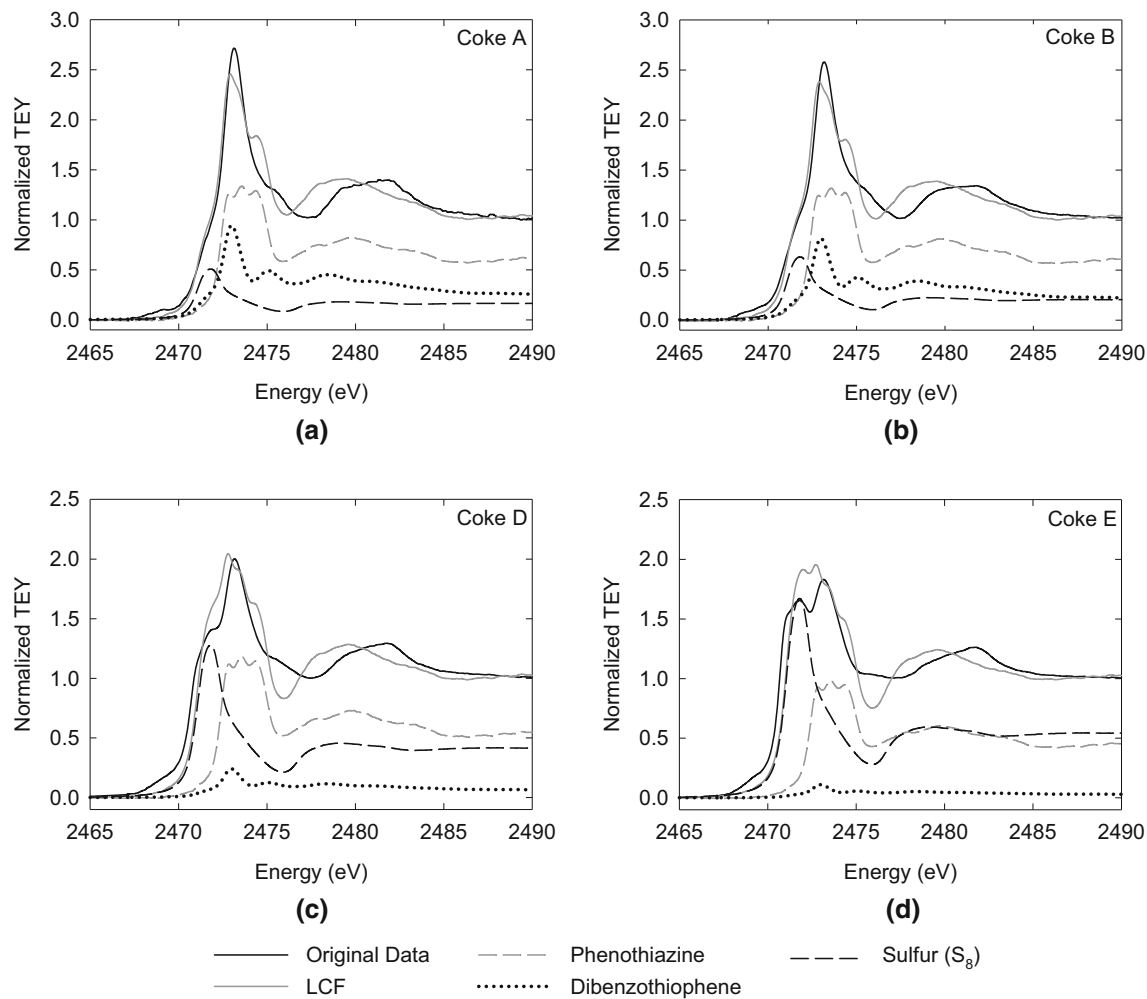


Fig. 6—Sulfur K-edge XANES spectra of the cokes fitted with two organic references and sulfur (S_8) of coke (a) A; (b) B; (c) D; (d) E. Note that the y-scales are different.

small. In addition, considering that this would be made up of several different metal sulfides, each with their own XANES spectrum, this is below the fitting capabilities in these samples. The detection limit for any particular component varies, and depends in particular on how different the spectrum of that component is to the other components present. In order to understand the contribution of the metal impurities to the sulfur speciation, the best method would be to measure XANES at the X-ray absorption edge for each metal.

The organic sulfur is present in complex aromatic compounds with the sulfur in a nominal oxidation state

of 0. Combined with the observations concerning S-S bound sulfur, the results presented here indicate that sulfur is present in the cokes in a fairly uniform oxidation state of 0, perhaps approaching a redox equilibrium during calcination. The XANES analysis for coke A, B, and C match very well with previous investigations on cokes,^[15,36] but the high amount of observed S-S bound sulfur (identified from S_8) as seen in cokes D and E has not been observed previously.

Sulfur in coke is usually described as organic aromatic compounds, but this may be based mostly on feedstock properties rather than a direct analysis of the coke. The

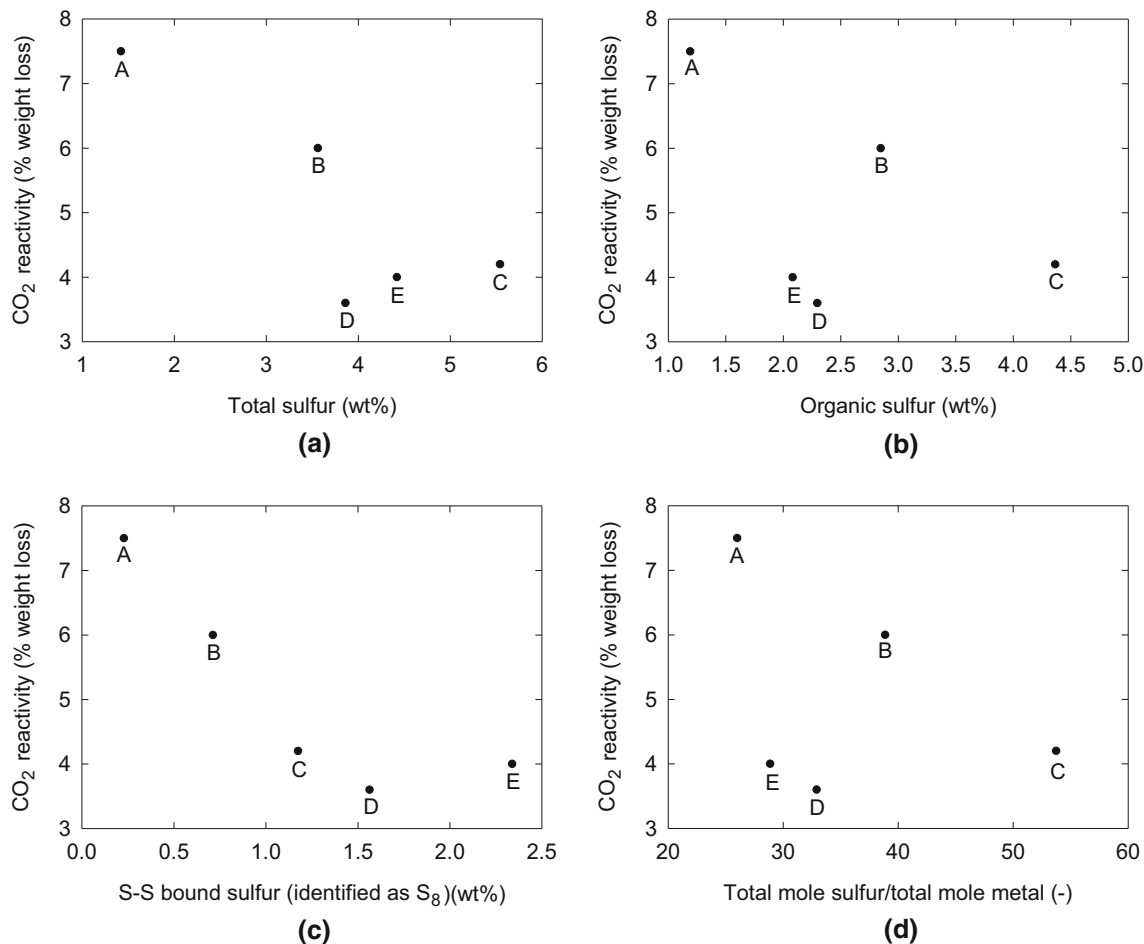


Fig. 7—The CO₂ reactivity of the cokes vs (a) total sulfur content; (b) organic sulfur content; (c) S-S bound sulfur content (identified as S₈); (d) sulfur/metal ratio.

XANES results give a possibility of the presence of S₈ in the coke, but the mechanism for the formation of this specie in the cokes is not well understood. A possibility is that S₈, or S_x ($x = 2, 4, 6$), is formed during high-temperature calcination in closed pores, which then is unable to leave the structure and is condensed after cooling to room temperature. Some possibilities for the mechanism at high temperature of the organic sulfur transformation to S_x have been proposed,^[17,26] but have not been verified experimentally (although significant amounts of sulfur were detected with SEM and EDS analysis in pores). The LCFs (Table III, Figures 5 and 6) give good fits to the edge for cokes A-C using S₈ as a component, while the small displacement of the edge in cokes D and E can be explained by an unidentified S species with a small displacement compared to S₈. This can be caused by the presence of condensed S_x, or other forms of S-S bonding (e.g., to carbon disulfides as C-S-S-C bonding and a small contribution of MeS₂).

The five cokes are from different producers, using crude oils with different composition, but all contain sulfur as a mixture of organic aromatic sulfur and S-S bound sulfur. The varying production and calcination processes therefore lead to similar sulfur chemistries.

The results from the linear combination fit (Table III, Figures 5 and 6) support previous work showing that thiophene-containing polycyclic aromatic hydrocarbons are the most stable after heat treatment.^[16] These may also contain some thiazines. Limited information can be obtained on the organic sulfur standards using the K-edge. For this differentiation between organic S species, the L-edge may be a better choice.

The organic compounds that were selected as standards are approximations for the chemical states that may be found within the cokes: sulfur contained in five and six member ring compounds with different levels of electron acceptor or donor strengths. However, it is not expected that the exact complex structure of S within the aromatic framework in cokes will be fully represented using pure reference compounds. The LCF indicates a larger portion of thiazines than anticipated, however, comparing the peak position and shape of the coke spectra in Figure 3(b) with the thiophene standard in Figure 3(a) it looks like a better correlation. More organic compounds were investigated in a previous study^[34] showing the diversity of the spectrum. It is difficult to confirm or deny if any one of these is the correct organic compound in this study. For the low-energy S-S components, the only possibilities are

the carbon disulfides (R-S-S-R). The precision regarding the division of S-S bonding and aromatic sulfur bonding achieved in this study seems to be very good.

The decreasing CO₂ reactivity with increasing S-S bound sulfur content for the five cokes observed in Figure 7(c) suggests that this kind of sulfur is involved in inhibiting the reaction of CO₂ with the coke. The much poorer relationship between CO₂ reactivity and organic S (Figure 7(b)) suggests that the organic sulfur does not play a large role in this inhibition. The effect of decreasing reactivity with increasing sulfur content is best understood in relation to the metal catalysts, which seems to be de-activated or passivated by the sulfur. As shown in Figure 7(d), the relationship between CO₂ reactivity, sulfur, and catalytic metals is complex. Cokes D and E have a higher total S content but lower sulfur/metal ratio than coke B caused by the high content of metals, as well as significantly lower CO₂ reactivity. This indicates that the sulfur in cokes D and E is more efficiently de-activating the metals than in coke B. A possibility is that condensed solid sulfur is present at pore walls, and that the pressure in the pores in combination with the high-temperature results in the film being intact and hinders the accessibility of metal catalysts. The exact mechanism for the inhibition was outside the scope of this study, but the S-S bound sulfur (identified from S₈) is the effective component and results in conditions in coke that hinder reactivity with CO₂. Provided that simpler methods can be developed for the identification of S-S bound sulfur, the results demonstrate the potential for significant reduction of the carbon consumption for the industry.

There are other considerations than CO₂ reactivity in selecting suitable coke blends for anode production. These include coke structure, total metal impurity content, specific metal impurity content, homogeneity, density, and porosity. As an example, using coke E in a mix with, e.g., coke A to reduce the CO₂ reactivity will lead to a high metal impurity content in the anode. This is undesirable because several of the metals will end up in the produced aluminum metal. The structure of coke E is also undesirable in anode blends because it may give a higher probability of the anode cracking due to a higher thermal expansion coefficient of isotropic cokes compared to anisotropic cokes. When comparing cokes B and D, with similar sulfur content and anisotropy, coke D might be preferred in industrial applications due to the much lower reactivity, at least if the vanadium level is low enough. Coke D may also be preferable to coke C, as the higher sulfur content does not give any decrease in the reactivity.

V. CONCLUSIONS

Industrial cokes varying with respect to levels of sulfur, metallic impurities, and isotropy were characterized by S K-edge XANES. Sulfur was found to be present as S-S bound sulfur, contrary to expectations, and complex organic (polycyclic thiophene and thiazines) compounds. The CO₂ reactivity of the cokes

showed a strong correlation between S-S bound sulfur content and CO₂ reactivity, showing that the presence of these sulfur species, rather than the total amount of sulfur, reduces the CO₂ reactivity. Identification of the components of sulfur that are important for reduction of reactivity is valuable for the optimization of coke blends for anodes for aluminum production, and will contribute to improved anode performance and a strategy to minimize SO₂ emissions, as well as CO₂ emissions.

ACKNOWLEDGMENTS

Financial support from the Norwegian Research Council and the partners Hydro, Alcoa, Elkem Carbon, and Skamol through the project “Reactivity of Carbon and Refractory Materials used in metal production technology” (CaRMA) is acknowledged. The cokes were provided by Rain Carbon, which also performed the CO₂ reactivity test. Research described in this paper was performed at the Canadian Light Source (CLS), which is supported by the Canadian Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. Beamline scientist Yongfeng Hu at CLS is acknowledged for his support to the XANES measurements.

OPEN ACCESS

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

REFERENCES

1. G. Djukanovic: *Int. Alum. J.*, 2012, vol. 88, pp. 26–30.
2. L. Edwards, N. Backhouse, H. Darmstadt, and M.-J. Dion: *Light Metals*, 2012, vol. 2012, pp. 1204–12.
3. L. Edwards: *JOM*, 2015, vol. 67, pp. 308–21.
4. A. Gomez and R. Heilgendorff: *Light Metals*, 2005, vol. 2005, pp. 535–38.
5. L. Edwards, F. Vogt, M. Robinette, R. Love, A. Ross, M. McClung, R.J. Roush, and W. Morgan: *Light Metals*, 2009, vol. 2009, pp. 985–90.
6. J.M. Hunt: *Petroleum Geochemistry and Geology*, 2nd ed., W. H. Freeman, New York, NY, 1996.
7. T. Reis: *Hydrocarb. Process.*, 1975, vol. 54, pp. 97–104.
8. M. Wang, L. Liu, J. Wang, L. Chang, H. Wang, and Y. Hu: *Fuel Process. Technol.*, 2015, vol. 131, pp. 262–69.
9. M. Kasrai, J.R. Brown, G.M. Bancroft, Z. Yin, and K.H. Tan: *Int. J. Coal Geol.*, 1996, vol. 32, pp. 107–35.

10. G.S. Waldo, R.M.K. Carlson, J.M. Moldowan, K.E. Peters, and J.E. Penner-Hahn: *Geochim. Cosmochim. Acta*, 1991, vol. 55, pp. 801–14.
11. S. Britto, M. Leskes, X. Hua, C.-A. Hébert, H.S. Shin, S. Clarke, O. Borkiewicz, K.W. Chapman, R. Seshadri, J. Cho, and C.P. Grey: *J. Am. Chem. Soc.*, 2015, vol. 137, pp. 8499–08.
12. M.E. Fleet: *Can. Mineral.*, 2005, vol. 43, pp. 1811–38.
13. I.J. Pickering, R.C. Prince, T. Divers, and G.N. George: *FEBS Lett.*, 1998, vol. 441, pp. 11–14.
14. D. Solomon, J. Lehmann, and C.E. Martínez: *Soil Sci. Soc. Am. J.*, 2003, vol. 67, pp. 1721–31.
15. S.J. Hay, J. Metson, and M.M. Hyland: *Ind. Eng. Chem. Res.*, 2004, vol. 43, pp. 1690–1700.
16. J. Xiao, Q. Zhong, F. Li, J. Huang, Y. Zhang, and B. Wang: *Energy Fuels*, 2015, vol. 29, pp. 3345–52.
17. Q. Zhong, J. Xiao, H. Du, and Z. Yao: *Energy Fuels*, 2017, vol. 31, pp. 4539–47.
18. Houston G.J., Øye H.A. (1985) *Aluminium* 61: 251–54, 346–49, 426–28.
19. M. Sørli: *Light Metals*, 1994, vol. 1994, pp. 659–65.
20. G.P. Gilmore and V.L. Bullough: *Light Metals*, 1982, vol. 1982, pp. 741–52.
21. P.J. Rhedey: *Light Metals*, 1982, vol. 1982, pp. 713–25.
22. S.S. Jones and R.D. Hildebrandt: *Light Metals*, 1979, vol. 1979, pp. 553–74.
23. K.N. Tran, S.K. Bhatia, A.J. Berkovich, and A. Tomsett: *Energy Fuels*, 2009, vol. 23, pp. 1909–24.
24. E.H. Hardin and C.L. Beilharz: *Light Metals*, 1991, vol. 1991, pp. 565–74.
25. S. Pietrzyk and J. Thonstad: *Light Metals*, 2012, vol. 2012, pp. 657–64.
26. J. Xiao, S.-Y. Deng, Q.-F. Zhong, and S.-L. Ye: *Trans. Nonferrous Met. Soc. China*, 2014, vol. 24, pp. 3702–09.
27. Y.D. Bensah and T. Fossnaes: *ARPJ. Eng. Appl. Sci.*, 2010, vol. 5, pp. 35–43.
28. S.M. Hume, W.K. Fischer, R.C. Perruchoud, J.B. Metson, and J.B. Baker: *Light Metals*, 1993, vol. 1993, pp. 535–41.
29. T. Eidet and J. Thonstad: *Light Metals*, 1997, vol. 1997, pp. 436–37.
30. T. Eidet, J. Thonstad, and M. Sørli: *Light Metals*, 1997, vol. 1997, pp. 511–17.
31. L.P. Lossius, I. Holden, and H. Linga: *Light Metals*, 2006, vol. 2006, pp. 609–13.
32. S. Rørvik, M. Aanvik, M. Sørli, and H.A. Øye: *Light Metals*, 2000, vol. 2000, pp. 549–54.
33. B. Ravel and M. Newville: *J. Synchrotron Radiat.*, 2005, vol. 12, pp. 537–41.
34. G.N. George and M.L. Gorbaty: *J. Am. Chem. Soc.*, 1989, vol. 111, pp. 3182–86.
35. G. Sarret, J. Connan, M. Kasrai, G.M. Bancroft, A. Charrié-Duhaut, S. Lemoine, P. Adam, P. Albrecht, and L. Eybert-Bérard: *Geochim. Cosmochim. Acta*, 1999, vol. 63, pp. 3767–79.
36. S.J. Hay: *The Formation and Fate of Carbonyl Sulfide (COS) Gas in Aluminium Smelting*, New Zealand, Auckland, 2002, pp. 47–105.