

## Reactivity of Coke in Relation to Sulfur Level and Microstructure

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### Abstract

The quality of coke materials available for anodes for the aluminium industry is changing and industrial cokes with higher impurity levels are now introduced. The cokes in the anodes must meet specifications with respect to impurity levels to ensure proper operation in the electrolysis cells, and a desired quality of the aluminium metal. The presence of sulfur has been observed to reduce the CO<sub>2</sub> reactivity and a certain level of sulfur is therefore targeted in the anodes. In this work, the significance of varying sulfur and metal impurity content in industrial cokes were evaluated with respect to CO<sub>2</sub> reactivity, accessible surface area, pore size distribution, surface oxide groups and crystallite reactive edge planes. While relatively similar cokes are observed to give a lower reactivity with increasing sulfur content, cokes that have distinct differences in surface properties can have dissimilar reactivity despite identical sulfur content. Correlations between pore size distribution and presence of S-S bound sulfur, possibly condensed S<sub>x</sub>, was also observed.

**Keywords:** Petroleum coke, Sulfur, CO<sub>2</sub> reactivity, Accessible area, Pore size distribution

### Introduction

In electrolytic production of aluminium, carbon is oxidized to CO<sub>2</sub> during the reduction of alumina (Al<sub>2</sub>O<sub>3</sub>). Prebaked anodes made of calcined petroleum coke, coal tar pitch and recycled anode butts provide the carbon for the reaction. The theoretical amount of carbon is 0.33 kg to produce 1 kg of Al, while in practice it is higher. This is caused by the back reaction, where produced Al is oxidized by CO<sub>2</sub> forming Al<sub>2</sub>O<sub>3</sub> and CO. The anode may also react with CO<sub>2</sub> or air. The air reactivity can be reduced by limiting the exposure to air by good covering of the anodes, which is well incorporated in modern cells. The reaction between produced CO<sub>2</sub> and carbon is assumed to be reduced by the presence of sulfur in the anodes.

In addition to the less dense coke materials produced by the refining industry, the cokes also have an increasing amount of sulfur and other metal impurities compared to previously used cokes [1, 2]. The changes in the quality of the petroleum coke will affect the performance of the anode in the pot room. An anode with more open porosity will be more susceptible to air and CO<sub>2</sub> reactivity, and many of the metals catalyse these reactions. A good overview of the effect of impurities can be found elsewhere [3]. Beside the possible increase in reactivity due to metals present in the coke, most metals end up in the finished aluminium product. Thus, the metal specifications for vanadium, nickel, iron and silicon in the anodes is usually decided by the tolerance level of these in the primary aluminium rather than the

increase in carbon oxidation. Sulfur is believed to have a positive effect on the carboxy reactivity, as high sulfur anodes has been shown to have a lower reactivity. The inhibiting effect caused by more sulfur comes at the expense of more SO<sub>2</sub> produced, and for plants without SO<sub>2</sub> scrubbing the sulfur content may be limited by SO<sub>2</sub> emission permission.

Sulfur and its effect on reactivity has been subject to many investigations, and it is assumed that the positive effect sulfur has on the CO<sub>2</sub> reactivity comes in combination with the metal impurities, as the effect of sulfur alone is possibly negative for both air and CO<sub>2</sub> reactivity when evaluating sulfur without other impurity interference [4]. The observed positive effect may be caused by the formation of inactive metal-sulfur complexes during carbonization [5, 6], however, most of the conclusions are based on adding impurity elements during the production of anodes. This will not necessary represent industrially produced anodes, as doped anodes may not have the same chemical state properly incorporated within the coke structure, which may give misleading results compared to the industrial cokes.

Sulfur speciation of selected cokes was previously performed by the authors by the X-ray absorption near-edge structure (XANES) technique [7]. Five cokes were investigated, which varied significantly with respect to content of sulfur (1.4 to 5.5 wt%) and content of metal impurities. Furthermore, there was a poor correlation between the sulfur content and CO<sub>2</sub> reactivity of some of these cokes. The ratio between S-S bound sulfur (which can result from elemental sulfur, pyritic sulfur and R-S-S-R sulfur) and other aromatically bound sulfur (e.g. thiophenes) varied significantly. The amount of S-S bound sulfur was found to inversely correlate with the CO<sub>2</sub> reactivity.

The aim of this work has been to gain an improved understanding of a wider range of factors that might affect the CO<sub>2</sub> reactivity of the cokes, like variations in reactive surface area of cokes of similar particle size, as well as variations in surface structure (i.e. ratio of edge to basal planes) or surface chemistry. Reactive surface area was estimated based on Hg intrusion porosimetry and N<sub>2</sub> adsorption experiments. The latter was also used for analysis of surface structure (ratio of edge, basal and defect sites). Possible differences in surface chemistry were also studied by monitoring the release of CO<sub>2</sub> and CO during heating.

## Materials and Method

Previously reported data and properties [7] of the five industrial cokes are summarized in Table 1. Impurity content (sulfur and metals) was measured by X-Ray Fluorescence (XRF), the optical texture evaluated by mosaic and fiber index found by light microscopy, and CO<sub>2</sub> reactivity reported as mass loss during a standard mass loss test (ISO-12981-1 Standard RDC-1141). The S-S bound sulfur found by XANES is reported as fraction of total sulfur content and wt%.

**Table 1.** Composition the five cokes. “Total metals” include V, Fe, Ni, Na, Mg, Al, Si and Ca.

	S (wt%)	S-S bound sulfur (fraction/wt%)	CO <sub>2</sub> reactivity (% mass loss)	Total metals (ppm)	Optical structure
Coke A	1.42	0.16 / 0.23	7.5	761	Anisotropic
Coke B	3.56	0.20 / 0.71	6.0	1323	Anisotropic
Coke C	5.54	0.21 / 1.18	4.2	1356	Anisotropic
Coke D	3.86	0.41 / 1.56	3.6	1668	Anisotropic
Coke E	4.42	0.53 / 2.34	4.0	2009	Isotropic

The same cokes were investigated for varying surface properties. An evaluation of the pore size distributions was done by two parallels of Hg intrusion porosimetry using AutoPore IV 9520 (from Micromeritics) on 1-2 mm coke particles (ASTM D4404-10). Hg is forced into pores where the force/pressure used will be equivalent to a pore size, the intrusion volume is measured and the Washburn equation is used to generate volume and size distributions (cylindrical pores are assumed) [8].

Nitrogen adsorption at  $-198.5\text{ }^{\circ}\text{C}$  was performed on the full relative pressure range (up to  $P/P_0 = 0.98$ ) on crushed coke particles  $<25\text{ }\mu\text{m}$  from the 1-2 mm fraction using a 3Flex 3500 Chemisorption Analyser (Micromeritics). Graphite powder (SLP30 from IMERYS) was used as a reference. The samples were degassed at  $300\text{ }^{\circ}\text{C}$  for 10 hours before analysis. The Barret-Joyner-Halenda (BJH) pore size distribution and area [9] were extracted from the software of the instrument. The adsorption data was used to find the relative contribution of edge:basal:defect sites based on a model established by Olivier [10] using density functional theory (DFT). Different adsorption potentials, expressed in kelvin (K), are used to account for the heterogeneity of the surface. For graphitic materials it is assumed that prismatic/edge sites are in the 20-49 K range, basal planes in the 50-60 K range, and higher energy regions of 61-100 K for defects [11]. Surface defects can be small, slit-like pores ( $<1\text{ nm}$  diameter), surface steps as well as attributed to surface groups. Two or three parallels were done on freshly crushed samples.

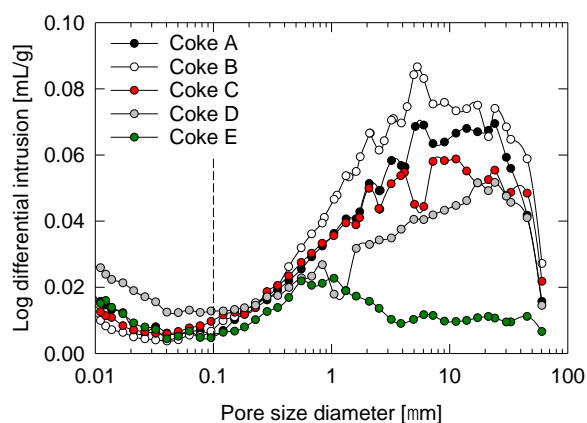
Surface oxides, assumed to be attached to edge sites, will decompose to CO and CO<sub>2</sub> during heat treatment. A rapid temperature ramping program with an analyser (ONH386 Series) from LECO was used. The CO and CO<sub>2</sub> is first detected by separate IR cells, to see what gases goes off when (and indirectly at which temperatures), while the total oxygen is found after the gas pass through heated copper oxide to convert CO to CO<sub>2</sub> and then to a separate IR detector. By comparing to graphite, oxygen assumed to be related to metal impurities, can be excluded from the surface oxides. Samples of 0.1 g crushed coke particles (particle size  $<25\text{ }\mu\text{m}$ ) from the 1-2 mm fraction were packed in tin capsules and the measurements were done by ramping of power linearly in the temperature range from 500 to 3,000  $^{\circ}\text{C}$  within 600 s. Two parallels of each coke and one from graphite powder were obtained.

The data obtained from Hg porosimetry, nitrogen adsorption and desorption and LECO oxygen analysis were combined and evaluated together with the previously obtained data presented in Table 1.

## Results and Discussion

### Hg intrusion porosimetry

The (smoothed) pore size distribution in the cokes (1-2 mm fraction) found by Hg intrusion is presented in Fig. 1. The measurements above  $60\text{ }\mu\text{m}$  are excluded in the analysis of intrusion volume, surface area and average pore size in Table 2 as it is likely a result of intrusion between grains, while data below  $0.1\text{ }\mu\text{m}$  is assumed affected by destruction of the grains at high pressures and is also excluded.



**Fig. 1.** Pore size distribution as a function of intrusion volume.

There are significant differences between the cokes. Coke E has the lowest intrusion volume and a centre around 1  $\mu\text{m}$ , resulting in a low total surface area. Coke D has a wider distribution and lower intrusion volumes than cokes A-C, resulting in low surface area compared to the other anisotropic cokes. Considering the region of pore diameters from 0.1 to 60  $\mu\text{m}$  the average pore size is decreasing steadily from A to E (Table 2) while the total pore area is highest for coke B.

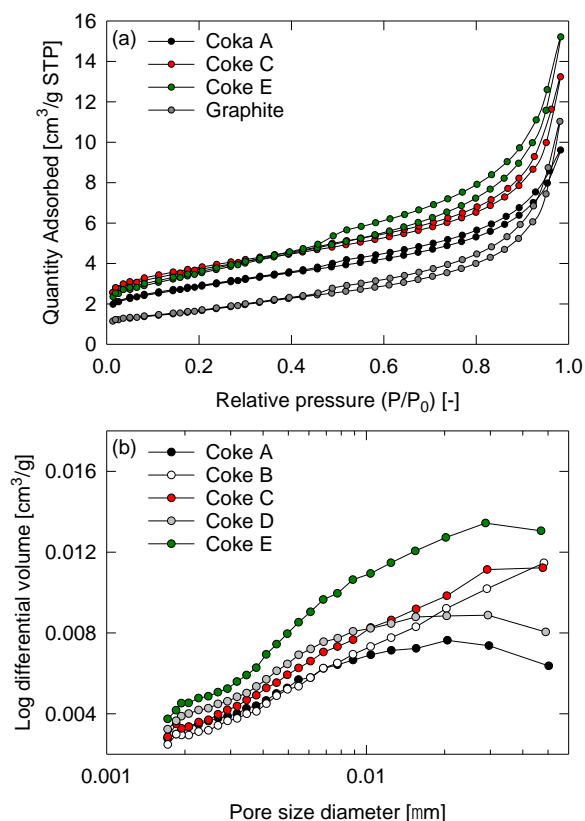
**Table 2.** The measured intrusion volume, estimated pore diameter and area for pores above 0.1  $\mu\text{m}$  and below 60  $\mu\text{m}$ , reference to Fig. 1.

	Intrusion volume [mL/g]	Area [ $\text{m}^2/\text{g}$ ]	Average pore diameter ( $d=4V/A$ ) [ $\mu\text{m}$ ]
Coke A	0.1222	0.268	1.83
Coke B	0.1363	0.311	1.75
Coke C	0.1091	0.289	1.51
Coke D	0.0899	0.257	1.39
Coke E	0.0039	0.174	0.90

The high increase in measured intrusion volume at high pressures, observed to be increasing nearing 0.01  $\mu\text{m}$  in Fig. 1 (and in fact increasing a lot in the range not presented), can be assumed to be affected by failure of the coke microstructure; at 10 nm the pressure is equivalent to 1.4 tons/ $\text{cm}^2$ . The method is insufficient at these pressures because the result reflects the integrity of the grains rather than the porosity. To investigate micro- and mesoporosity in cokes, Hg intrusion porosimetry is clearly not the best option. This range needs to be evaluated further with other methods, for example pore size distributions obtained by  $\text{N}_2$  adsorption.

#### Nitrogen adsorption

Nitrogen adsorption and desorption isotherms are shown in Fig. 2a for a selection of the cokes and the graphite. The isotherms resemble the type II isotherms defined by IUPAC [12], usually observed for non-porous and macroporous materials. The change to the linear middle section corresponds to the change from monolayer to multilayer adsorption, and the graphs increase without limit close to  $P/P_0=1$ . There is a small hysteresis observed and the sharp step-down of the desorption branch is observed approximately at  $P/P_0\sim 0.4-0.5$ . This is defined as a H4 hysteresis loop, often observed for carbons with pore structures including several different pore sizes in the network (micro- mesoporous carbons). H4 can also be related to slit-shaped pores and microporosity. This behaviour is expected for petroleum cokes. All the cokes and the graphite have this hysteresis, but for coke E the relative difference between adsorption and desorption in the linear hysteresis area was larger than the other cokes. Cokes B and C had the smallest hysteresis.



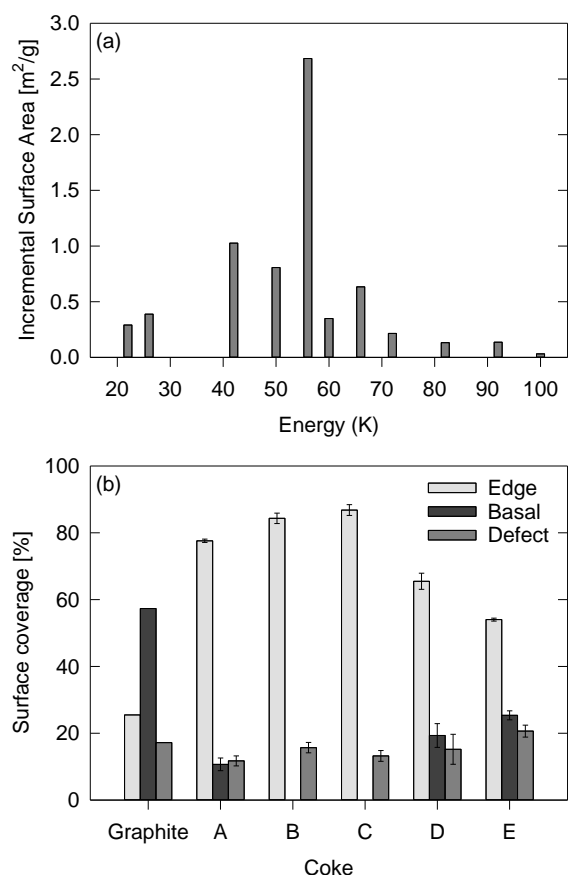
**Fig. 2.** (a) Isotherms for cokes A, C, E and graphite, showing the quantity of N<sub>2</sub> adsorbed at varying relative pressures ( $P/P_0$ ), (b) BJH pore size distribution.

The BJH adsorption pore size distribution in the mesopore area, with pore sizes between  $\sim 2$  nm and 50 nm, is presented in Fig. 2b. According to the results, coke A has the least amount of small pores, and coke E has more small pores than the other cokes. At the lowest pore size range, cokes A, B and C are quite similar, but variations are observed from  $\sim 4$  nm. N<sub>2</sub> adsorption is a non-destructive method, and the behaviour of the cokes of pore sizes below  $0.1 \mu\text{m}$  do not reflect the observations from mercury intrusion, which was clearly affected by cracking of grains at high pressures. The isotropic coke has more pores in the entire range below  $0.1 \mu\text{m}$  than the other cokes, as seen from Fig. 2b, which confirm this theory. The BJH method use the Kelvin equation in combination with the t-curve (carbon black defined solid) and are known to under-estimate contribution from narrow mesopores, indicating that the method is not suited for determining specific differences for pore sizes below 5-10 nm.

The complete picture of the porosity of the cokes are still not established combining Hg porosimetry and N<sub>2</sub> adsorption. It is expected that the Hg porosimetry gives reliable data above  $0.1 \mu\text{m}$ , and significant differences between the cokes are observed, while the isotropic coke E has a significantly smaller average pore size than the rest of the cokes. N<sub>2</sub> adsorption also shows this coke has a larger contribution of pores down to  $0.01 \mu\text{m}$ . A better analysis of the even smaller pores may be investigated using molecular simulations or DFT given a good model system supported by sufficient experimental data, but was beyond the scope of this study.

The surface coverage of edge, basal and defect area were determined by nitrogen adsorption combined with a DFT model in the software. A typical plot of the distribution of incremental surface area vs. energy is presented for graphite in Fig. 3a, where both the typical edge site energy (42 K) and basal plane energy (58 K) can be observed. The summarized result of the areas assumed to be edge, basal and defect sites for graphite and cokes are presented in Fig. 3b. All cokes have a high portion of edge sites compared to graphite. For cokes A to C the portion of edge sites are increasing with increasing sulfur

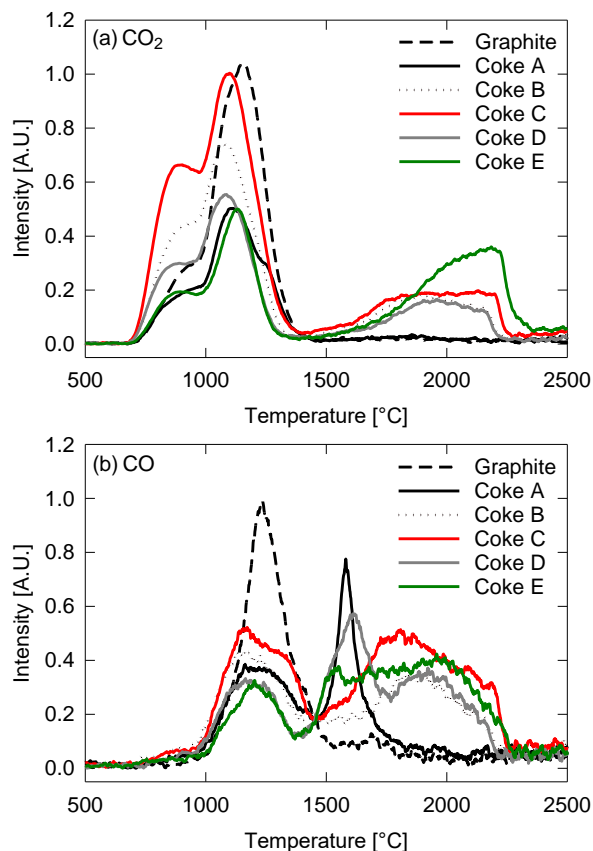
content (which increase from A to C), while cokes D and E have a significantly lower portion of edge sites. Both defect sites and edge planes indicate insufficiencies in the carbon material and less ordered structure. Coke D and E appear to have more of the non-reactive basal planes.



**Fig. 3.** (a) Typical plot of incremental surface area vs. energy for graphite, and (b) edge site, basal planes and defect sites surface coverage of graphite and industrial cokes A-E. Error bars for the cokes show one standard deviation where  $n=3$  for cokes A-D and  $n=2$  for coke E.

### Surface and metal oxides

Information about the content of oxides in the cokes, obtained by combustion coke to CO and CO<sub>2</sub> measured by a LECO oxygen analyser, is presented in Fig. 4 and Table 3. The total amount of oxygen varies from 0.128 wt% in coke A, to 1.07 wt% in coke C. Comparing release of CO<sub>2</sub> for graphite and cokes in Fig. 4a it is clear that all but coke A have one or several additional peaks above 1450 °C. A similar limit is found in the release of CO in Fig. 4b. By separately integrating the CO<sub>2</sub> and CO graphs, one can find the oxygen related to surface oxide groups assumed to be present below 1450 °C, and oxide related to metal oxides as the higher temperature peaks. Release of CO<sub>2</sub> from coke is an indication of carboxylic, anhydride and lactone groups, while phenol, carbonyl, anhydride, ether and quinone groups give rise to CO gas [13]. Below 1450 °C both CO<sub>2</sub> and CO peaks appear to be similar but with different intensities (the intensity do not reflect the actual amount of oxygen). Based on these results, no significant differences in the surface chemistry of the cokes could be detected, although the ramping of power (temperature) is far too high for detection of specific surface compounds. The technique is mostly used to find the total amount of oxygen in materials.



**Fig. 4.** Evolved (a) CO<sub>2</sub> and (b) CO from combusted oxides in cokes and graphite.

**Table 3.** The oxygen content in the cokes. The evaluation of surface oxides originates from data obtained below 1450 °C.

	Total oxygen (wt%)	Oxygen as CO <sub>2</sub> (wt%)	Oxygen as CO (wt%)	CO:CO <sub>2</sub> for surface groups
Graphite	0.132	0.057	0.075	1.1
Coke A	0.128	0.040	0.088	1.2
Coke B	0.578	0.060	0.518	5.1
Coke C	1.07	0.081	0.989	6.2
Coke D	0.652	0.053	0.599	5.3
Coke E	0.877	0.074	0.803	2.9

Cokes B, C and D all have more than 5 times more CO than CO<sub>2</sub> and coke E has 3 times as much. This indicates that phenol, carbonyl, anhydride, ether and quinone surface groups are dominating in the cokes. From the CO:CO<sub>2</sub> ratio we observe that the cokes A and E, which also have relatively high reactivities when the active area is accounted for (see Fig.5), also have very low CO:CO<sub>2</sub> ratios, while the cokes B, C and D have similar CO:CO<sub>2</sub> ratios and also lower, and relatively similar CO<sub>2</sub> reactivity. It is however, beyond the scope of this work to verify and gain a better understanding of these apparent correlations, and more experiments, preferably with a slower heating rate and a wider choice of cokes would be needed.

#### Evaluations of CO<sub>2</sub> reactivity

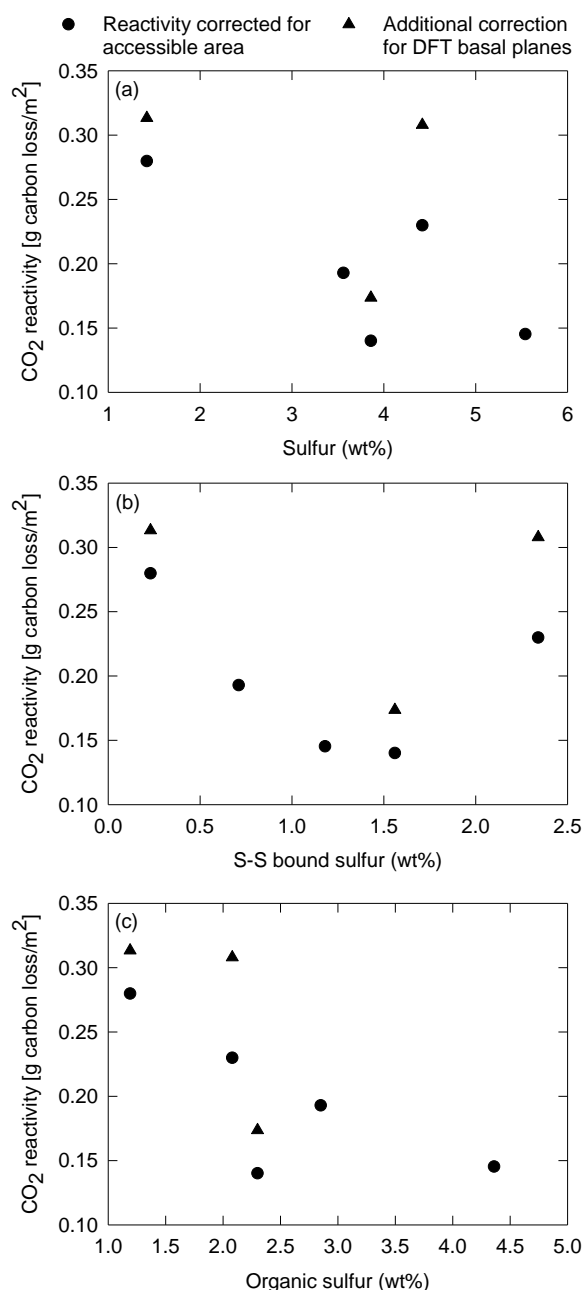
The CO<sub>2</sub> reactivity will depend on the surface area accessible for the reaction between CO<sub>2</sub> and C, where diffusion of the CO<sub>2</sub> into the pores is of high importance. Although the small pores contribute to

a larger surface area, transport of CO<sub>2</sub> gas is limited and the pore walls are thus not accessible for the reaction to a significant extent. In large pores, the mass transport can be described by the conventional binary diffusion coefficient, but when the pore size approach the mean free path of the CO<sub>2</sub> molecules, the slow Knudsen diffusion quickly starts to dominate [14]. The test was done on at 1000 °C and 0.2 MPa, where the mean free path ( $\lambda$ ) for CO<sub>2</sub> is 365 nm. Knudsen diffusion is said to be dominant when  $K_n > 10$  and negligible when  $K_n < 0.1$ , where the so-called Knudsen number is defined as  $K_n = \lambda / d_p$ , where  $d_p$  is the pore diameter. This means that pores below approximately 40 nm does not contribute to the reactive area as the total diffusion here is very low. The total diffusion constant is a function of both the (constant) mass diffusion constant  $D_{ab}$ , approximately 1.1 cm<sup>2</sup>/s for a CO<sub>2</sub>-CO binary system at the given conditions using the Slattery-Bird correlation [15], and Knudsen diffusion constant  $D_K$ , proportional to  $d_p$ , by

$$\frac{1}{D_{tot}} = \frac{1}{D_{ab}} + \frac{1}{D_K}$$

Assuming pore diameters larger than 0.1  $\mu\text{m}$  (i.e. corresponding to the region where we have reliable Hg intrusion data),  $D_{tot}$  decrease with more than 80 % compared to a situation where  $D_{ab}$  dominates (i.e. no or large pores). The calculated surface area, excluding pore sizes  $< 0.1 \mu\text{m}$ , was used to normalize the CO<sub>2</sub> reactivity data in Fig. 5, however, moving the included range to higher pore sizes do not result in a significant difference in the observed trends. All but coke E have a relatively similar pore size distribution above 0.1  $\mu\text{m}$ , and thus the reactivity of coke E is the only one that will change notably compared to cokes A to D. Fig. 5 shows the reactivity with respect to total sulfur content, S-S bound sulfur and organic sulfur, and cokes A, D and E is also normalized to subtract the coverage of basal planes found by DFT (no basal planes were found for B and C).

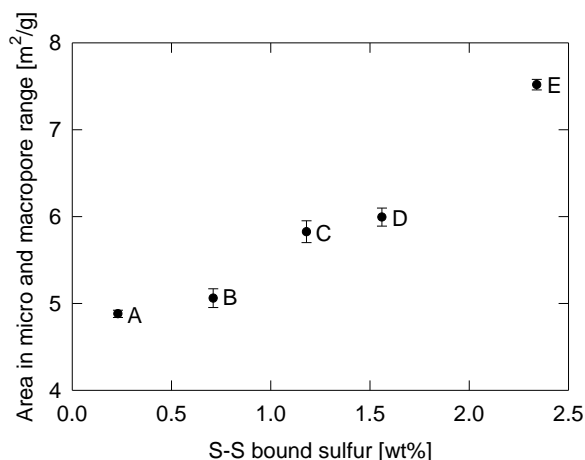




**Fig. 5.** The normalized reactivity, with area corresponding to pore size  $>0.1 \mu\text{m}$  and possible exclusion of basal planes, plotted with respect to (a) total sulfur, (b) S-S bound sulfur and (c) organic sulfur. Note that the y-value of each coke is identical in all figures, only the sulfur amounts vary (Table 1).

Based on Fig. 5, the differences originally observed in mass loss during the reactivity test is likely due to differences in the available area for the reaction to occur. With the exception of coke E, decreasing reactivity with more sulfur, S-S bound sulfur and organic sulfur was observed. Comparing Fig. 5a to 5c, it appears that the correlation of lower reactivity and S-S bound sulfur previously observed may be indirect. Fig. 6 show that the amount of S-S bound sulfur follow the area for pores  $<50 \text{ nm}$  (found by BJH adsorption data), which may also explain the presence of S-S bound sulfur, as many compounds containing S-S bonds (elemental sulfur for example), is not expected to be stable at the typical calcination temperatures. If S-S bound sulfur is present in the smaller pores, and these are not accessible for the  $\text{CO}_2$  reaction, the S-S bound will not contribute to the inhibiting reaction. The proper chemistry of this S-S compound is still unknown, but  $\text{S}_x$  ( $x=2,4,6$  and  $8$ ), formed from organic sulfur in pores,

trapped in small pores during heat treatment and subsequently condensed, have previously been discussed as an option [4].



**Fig. 6.** The relationship between area in the BJH evaluations (2-50 nm) and the S-S bound sulfur.

Regarding the cokes A, B and C, these cokes have similar surface areas and pore size distribution, the N<sub>2</sub> adsorption isotherms are similar and the DFT analysis gave almost complete surface coverage of reactive sites. The largest observed difference was coke A on the BJH pore size distribution and the oxygen surface groups. The intermediate step of CO<sub>ads</sub> formation in the Boudouard reaction may also be affected by the differences in the oxygen surface groups between the cokes, but these were observed to be similar in all cokes. Coke D and E were also shown to have a different pore size distribution explaining the low reactivity, as narrow pores are inaccessible for the reacting gases compared to the outer surface area/wide pores. A higher portion of the non-reactive basal planes was also observed in these cokes. The sulfur content, in practice the organic sulfur content, seems to be correlated to the lowering of reactivity in high-sulfur cokes, as S-S bound sulfur, possibly condensed S<sub>x</sub>, is most likely trapped in narrow pores.

## Conclusions

Selected cokes were investigated with respect to porosity, pore size distribution, surface chemistry and surface structure, and the investigations gave a better insight in different factors affecting CO<sub>2</sub> reactivity in cokes. Poor correlations between the reactivity and the amount of sulfur present in the cokes could be explained by the accessible surface area. The isotropic coke also has a much lower average pore size and a large amount of pores in the micro and macroporous range than the rest of the cokes, which can result in low structural integrity of the grains. Higher amount of S-S bound sulfur is observed in the cokes with smaller average pore size, indicating that any correlating relationship between S-S bound sulfur and CO<sub>2</sub> reactivity might be indirect.

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