

A SIZE-DEPENDENT THERMODYNAMIC MODEL FOR THE CARBON/HYDROGEN/SULFUR SYSTEM IN COKE CRYSTALLITES: APPLICATION TO THE PRODUCTION OF PRE-BAKED CARBON ANODES

Philippe Ouzilleau, Aïmen E. Gheribi and Patrice Chartrand

CRCT (Center for Research in Computational Thermochemistry), Department of Chemical Engineering, École Polytechnique, P.O. Box 6079; Downtown, Montréal, Québec, H3C3A7, CANADA

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Abstract

Changes in the quality of green cokes available for the production of pre-baked carbon anodes used in the production of aluminum are stimulating the development of a better understanding of the thermodynamic behavior of cokes. Impurity content and crystallite sizes (over a wide range of temperature) are of particular concern. No thermodynamic model currently exists for the precise prediction of the enthalpy and entropy of cokes that can be applied to industrial processes. The present model uses a simplified structure for coke crystallites for the production of predictive calculations that can potentially incorporate the impact of various impurities. The thermodynamic properties of coke crystallites as functions of temperatures, crystallite sizes and hydrogen/sulfur contents are presented in this work. Examples of key applications of the present model are: the calculation of dehydrogenation/desulfurization curves of cokes with constrained L_c and of the gaseous composition of volatile species emanating from heat treated cokes.

Introduction

Carbon materials are essential components of the Hall-Heroult process for the production of aluminum, especially for pre-baked anodes. The use of carbon is not limited to pre-baked anodes in the Hall-Heroult process. For example, carbon is closely linked to the use of Söderberg anodes and the production of carbon cathodes. However, significant quantities of carbon materials are continuously required for the production of pre-baked anodes used in the Hall-Heroult process. Also, the production process for these pre-baked anodes is dependent on many complex parameters that are often difficult to control (for example, the evolution of sulfur during heat treatment [1]). The most important industrial carbon materials used are found in the form of cokes. The chemical composition and crystalline structure of cokes are dependent on the base material and on the transformation process used to produce the final carbon material. In recent years, important changes in the overall quality of available cokes used in the production of the pre-baked anodes are stimulating the development of a better understanding of the thermodynamic behavior of cokes over a wide range of temperatures [2]. It is expected that this better understanding, combined with a detailed kinetic analysis of the processes concerned, will result in improved carbon-using processes related to the aluminum industry.

According to IUPAC (International Union of Pure and Applied Chemistry) recommended terminology [3], coke is defined as a high carbon content solid possessing a graphitizable crystalline structure after a given high temperature heat treatment. In the aluminum industry, most cokes are of petrochemical origin [4].

Hence, the properties of the available cokes are closely related to the evolution in the quality of available petroleum products. The effects of key impurities on the properties of cokes are already known. For example, it is reported [4] that green cokes possessing higher initial hydrogen content will produce more porous calcined cokes. However, sulfur is by far the most damaging impurity for the use of cokes. During the production of anodes, calcined cokes produced from high sulfur green cokes are characterized by a lower density, higher air reactivity and a higher porosity [2, 5, 6]. All these parameters are critical for an economically and environmentally responsible operation of the Hall-Heroult process. In the last decade, the use of high-sulfur cokes has become more common in the industry, due to their greater availability [2, 7].

Due to the major problems associated with the use of high-sulfur cokes, a great deal of experimental research is devoted to the elaboration of various desulfurization processes applicable to cokes. A previous review discusses the most studied desulfurization processes [8]. Of all the possible transformations, the desulfurization process, following a given high temperature heat treatment, is the most studied. The industrial viability of such a process has however not been demonstrated. For example, a previous empirical study on the subject of thermal desulfurization concludes that the various approaches explored so far are unlikely to result in the production of satisfactory thermal desulfurization [1]. It is stated in a previous work that the lack of a reasonable thermodynamic model for cokes is preventing the development of a suitable thermal desulfurization process [8].

In the present work, a thermodynamic model for the crystalline portion of cokes (*i.e.* coke crystallites) is presented. This new model is innovative in the sense that it readily allows the calculation of both the relative enthalpy (H) and absolute entropy (S) of coke crystallites for various impurities (hydrogen and sulfur for the moment). It takes into account crystallite size parameters such as the experimental measured crystallite stack height L_c and L_a , the crystallite plane diameter [9]. Using the FactSage software [10], solid/gas “pseudo-equilibrium” calculations can be performed with Gibbs energy minimization from estimated enthalpy and entropy of coke ($G=H-T\cdot S$). It is important to note that the present model is entirely predictive and does not use fitting parameters, as is typically the case in other thermodynamic models [11].

Thermodynamic model for coke crystallites

The coke crystallite model is a new thermodynamic model based on notions of physics, thermodynamics and organic chemistry. The details of the model will not be discussed here. The coke crystallite model applied to the carbon/hydrogen (C-H) system

was presented in details in our previous work [12]. The application to the carbon/sulfur (C-S) system is also presented in another work [13].

The general model is based on the following main hypotheses:

- 1) The geometric configuration of crystallites is simplified in such a way that it is solely defined by the values of L_a and L_c . All crystallites are assumed to have the same values of L_a and L_c .
- 2) The extensive thermodynamic properties (enthalpy, entropy and Gibbs energy) are determined by L_a and L_c .
- 3) Thermodynamic paths from defined reference states (C(graphite), H(gas) and S(gas)) can be used to estimate the properties of the chemical species composing the crystallites.
- 4) The bulk of the crystallite is solely occupied by carbon atoms. Sulfur and hydrogen atoms are located on the surface of the crystallites (as sublattice species).

As an added simplification to allow a quick comparison of model predictions and experimental data, it is considered that the height of the stacked planes of the crystallite (L_c) is approximately equal to the width (L_a) of the crystallite planes ($L_c \approx L_a$). This approximation was used in previous work for the physical simulation of XRD measurements of graphitic crystallites [14]. The geometry of the crystallite according to the present model is presented in Figure 1.

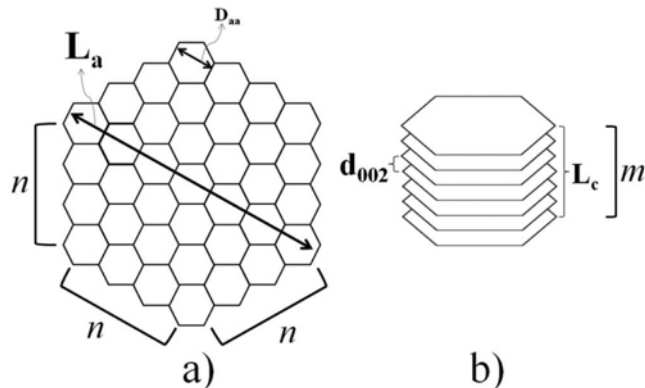


Figure 1. Geometry of the idealized crystallite

In Figure 1, L_a and L_c give the dimensions of the assumed crystallite geometry, D_{aa} is defined as the graphite lattice constant (at 298.15K and 1 atm) for a-a carbon atoms. The value of D_{aa} is 0.2461 nm [15], d_{002} is the interplanar distance, m is the number of stacked plane and n is the number of hexagonal sites present on each side of the crystallites ($n = 4$ in Figure 1). The model assumes that a given integer value of n is associated with a predefined range of L_a (relationship given in Eq. 1).

$$(L_a)_n = D_{aa-lattice} \cdot ((2 \cdot n) - 1) \quad (1)$$

In practice, if we define a value of L_a (or L_c , since $L_c \approx L_a$), it is possible to associate the properties of the crystallite with a crystallite possessing a geometry defined by a given n . Eq. 1 is applicable for values of L_c greater than 1.23 nm ($n \geq 3$). To define the thermodynamic properties of the crystallites, it is necessary to divide the hexagonal sites of the crystallite planes into three different types (i.e. three sublattices). This division is based on the difference between the properties of armchair and zigzag

configuration of graphene edge structures [16, 17]. This division is presented in Figure 2.

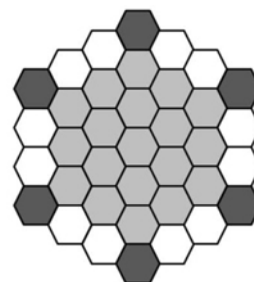


Figure 2. Definition of the three sublattices in an idealized crystallite plane for $n = 4$: C₄₃ sites (dark gray), C₅₄ sites (white) and C₆₆ sites (light gray)

For a given value of n ($n = 4$ for example in Figure 2), the number of each type of site is defined by mathematical equations defined in our previous work [12, 13]. The nomenclature (C₄₃, C₅₄ and C₆₆) used for naming these sites is also presented in these works [12, 13]. The detailed structure of these chemical species is based either on previous experimental/theoretical work [16, 17, 18, 19] or on reasonable assumptions.

Different types of chemical species, with or without S and H, are allowed to mix on the C₄₃ and C₅₄ sites (Figure 2). Each one has an enthalpy and entropy derived from thermodynamic paths related to the known reference states. Finally, the FactSage software [10] is used to perform Gibbs energy minimization calculations to determine the thermodynamic equilibrium between the coke crystallites and various chemical compounds for different temperatures, pressures and crystallite sizes L_c .

Results and discussion

Previous work focused on the carbon/hydrogen [12] and on the carbon/sulfur [13] systems. Key results previously used to validate the present approach are presented in Figure 3 and Figure 6. New results, pertinent to the aluminium industry, are presented in Figures 4 to 5 and in Figure 7 to 8.

The carbon/hydrogen binary system

The results for the carbon/hydrogen system are discussed in greater detail in our other work [12]. The results presented in Figure 3 give an overview on how the model was validated with available experimental data. In Figures 4 and 5, new results are presented for the predicted evolution of the gas phase composition in the carbon/hydrogen system for various temperatures and crystallite sizes.

For the C-H system, two phases are considered for the equilibrium calculations: the coke crystallites and the gas phase containing a selected number of chemical compounds. The condensed volatile matter phase is not included in the presented results. For the results presented in Figures 3 to 5, the composition of the gas phase is simplified to H₂(g), CH₄(g) and chrysene (C₁₈H₁₂(g)). This choice is based on previous experimental work on the kinetic study of the emission of volatile matter observed during experimental heat treatment of cokes [20, 21]. The thermodynamic properties of H₂(g), CH₄ and C₁₈H₁₂(g) are taken from previous work [22, 23].

The predictive calculations of the present model are compared in Figure 3 to dehydrogenation experimental results [6, 24, 25] where various cokes are heat treated to a given temperature using a specific heating process.

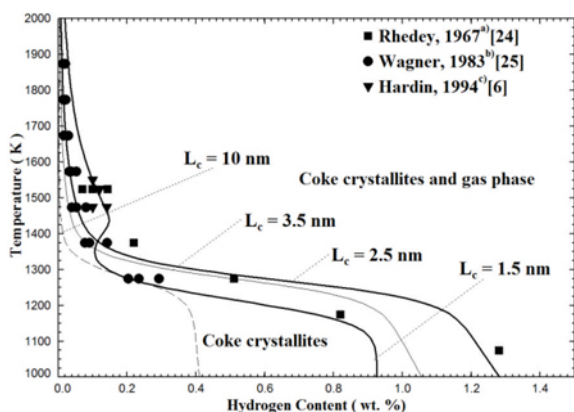


Figure 3. Comparison of the predicted dehydrogenation of idealized coke crystallites of fixed L_c values under gas equilibrated condition with experimental data ($P_{\text{total}} = 1 \text{ atm}$)

- a) Reported L_c values between 1.50 and 1.72 nm up to 1373 K and between 1.94 and 2.25 nm at 1523 K; b) Estimated L_c values between 1.75 to 2.15 nm for temperatures between 1200 and 1473 K and over 2.214 nm at temperatures over 1500 K [26]; c) Reported L_c values between 2.60 and 3.05 nm for the temperature range of 1473 to 1550 K

A good agreement can be seen between the reported experimental dehydrogenation and the predicted dehydrogenated curves calculated by the present model. The quality of the agreement is dependent on various factors as detailed in our previous work [12]. One example is the requirement that the heating process must be slow enough so that the assumption of thermodynamic equilibrium during the entire heating process is valid. Despite any restrictive factor, it is interesting to see that the model is still valid for the prediction of dehydrogenation behavior. Another interesting result that can be obtained from the present model is the change of the gas phase chemical composition in the “Coke crystallites and gas phase” region of Figure 3. These results are presented in Figures 4 and 5.

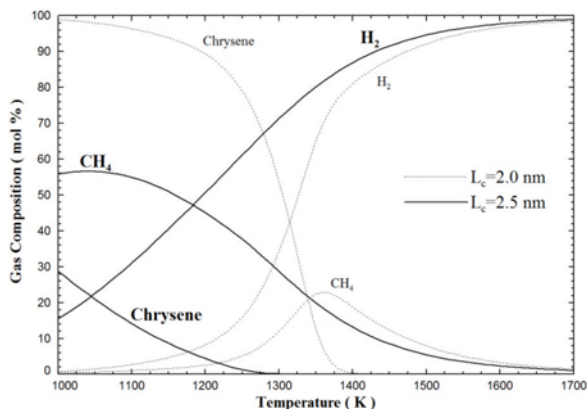


Figure 4. Evolution of the gas phase composition at thermodynamic equilibrium with temperature in the carbon/hydrogen system for values of $L_c < 2.7 \text{ nm}$ (n equal or smaller than 5 in Eq. 1)

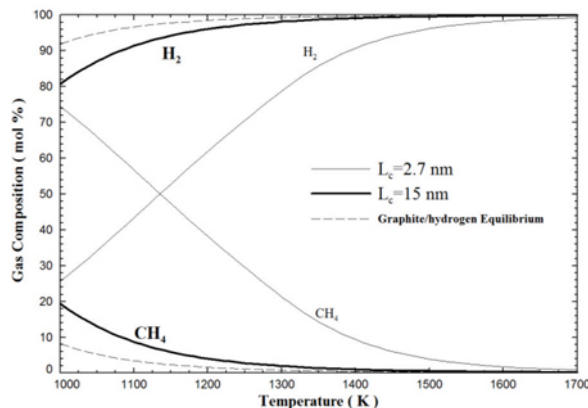


Figure 5. Evolution of the gas phase composition at thermodynamic equilibrium with temperature in the carbon/hydrogen system for values of $L_c \geq 2.7 \text{ nm}$ (n greater than 5 in Eq. 1)

In Figure 4, it can be seen that the composition of the gas phase is approximately in agreement with observations made during a previous kinetic study [20] of the thermal degassing of hydrogenated species in cokes. The general behavior is that condensable species (approximated as chrysene) are volatilized first, followed by methane and finally by hydrogen. It can also be seen that the growth of crystallites favors the formation of H_2 over CH_4 and chrysene. At $L_c = 15 \text{ nm}$, the gas phase composition is quite close to the equilibrium $\text{C}_{\text{graphite}} + 2 \text{H}_2(\text{g}) \leftrightarrow \text{CH}_4(\text{g})$. This aspect is explained by the fact that larger crystallites are more stable if the value of L_c is higher according to the present coke crystallite model and they contain much less surface sublattice sites ($\text{C}_{43} + \text{C}_{54}$) relative to bulk sublattice sites (C_{66}).

When comparing Figures 4 and 5, it can also be seen that the formation of chrysene is not predicted to occur if the L_c value of the crystallites is above $\sim 2.7 \text{ nm}$ (n greater than 5). This is due to the fact that the stability of hydrogenated crystallites is greater for crystallites with higher values of L_c . From our calculations, it is possible to conclude that the stability of chrysene relative to the idealized coke crystallites is directly correlated with the measured value of L_c . The validity of this prediction for the use of cokes in the aluminum industry is yet to be verified as other factors must be taken into account for the simulation of industrial cokes. For example, industrial cokes generally contain a non-negligible amount of sulfur.

The carbon/sulfur binary system

The results of the carbon/sulfur systems are discussed in greater detail in our previous work [13]. Figure 6 gives an overview on how the model was validated for the carbon/sulfur system using critically evaluated coke desulfurization data. Figure 7 presents new results for the predicted evolution of the gas phase composition in the carbon/sulfur system.

For the C-S system, the equilibrium is assumed to consist of coke crystallites and a gas phase containing carbon/sulfur chemical compounds. The gas phase composition for the results presented in Figure 6 is simplified to a limited number of gaseous compounds. These compounds are $\text{CS}(\text{g})$, $\text{CS}_2(\text{g})$ and $\text{S}_2(\text{g})$. The thermodynamic properties of these compounds are taken from a previous assessment [22].

The predictive calculations can be compared to experimental results concerning the high temperature removal of high sulfur content cokes. However, since the system studied is limited to the carbon and sulfur atomic species, the results can only be reasonably compared to measurements above 1500 K as it is reported that the hydrogen content of cokes treated above 1500 K is typically less than ~0.1 wt. % [6, 24], which is in agreement with Figure 3. However, this temperature limit necessitates precise knowledge of the L_c value of the coke heat treated at temperatures above 1500K due to the faster graphitization kinetics above 1500K [27].

Several experimental studies on the thermal desulfurization of cokes are available in the literature [28, 29, 30, 31, 32]. However, only a handful of reports can be compared rigorously to the model results [5, 6, 33, 34, 35, 36]. To make a valid comparative analysis, the final structure of this heat treated coke must be primarily composed of graphitic crystallites and it is required that the cokes are of low ash contents. Further details are given in our previous work on the reasons for these specific comparative conditions [13]. A simplified comparative analysis between the predicted desulfurization and the experimental measurements is shown in Figure 6.

It can be seen that the agreement between the reported measurements under atmospheric pressures and the model calculations is very good. In our previous work focusing on the carbon/sulfur system [13], the extension of the number of chemical compounds in the gas phase had little effect on the results compared to the calculations presented in Figure 6. Also, a comparative analysis was presented in our previous work for measurements made under low pressure (~0.4 atm) for the experimental work of Brandtzaeg et al. [34, 35, 36].

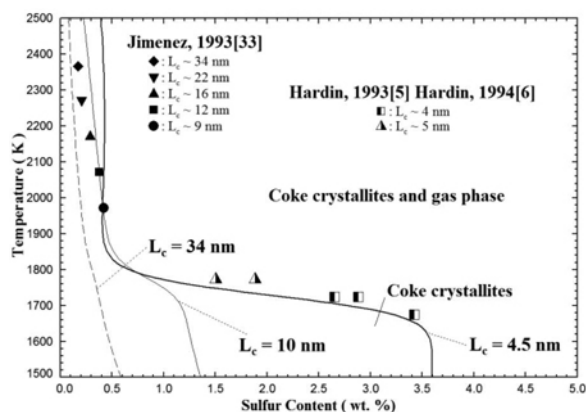


Figure 6. Comparison of the predicted sulfur removal during the heat treatment of cokes under gas equilibrated condition with experimental data ($P_{\text{total}} = 1 \text{ atm}$)

The evolution of the gas phase composition in equilibrium with coke crystallites is presented in Figure 7. It is possible to observe that, for greater values of L_c , the molar % of gaseous compounds containing carbon free gas (*i.e.* S_2 in this particular case) is greater when compared to the smaller L_c case. Coke crystallites characterized by large values of L_c are thermodynamically more stable due to the lesser importance of surface energy (when compared to smaller crystallites). Larger crystallites possess a smaller surface/volume ratio. Overall, carbon atoms in larger crystallite are less available for the formation of carbon/sulfur gaseous species.

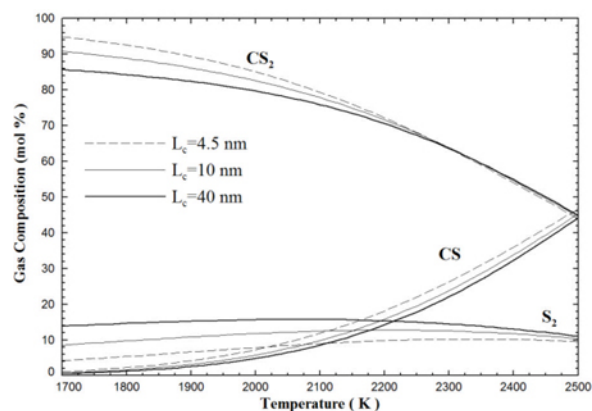


Figure 7. Evolution of the gas phase composition at thermodynamic equilibrium with coke crystallites in the carbon/sulfur system for three values of L_c

Preliminary notes on carbon/sulfur/hydrogen system

The application of the model to the simulation of the heat treatment of green cokes and the production of pre-baked anodes would be valuable for the aluminum industry. However, some aspects of the model restrain the strict application of the coke model in its application. Some examples are discussed below.

During the calcination of green cokes, the heat treatment temperatures are usually below 1500 K [37]. The thermodynamic system studied should be the carbon/hydrogen/sulfur ternary system, as this temperature range is below the temperature limit of 1500 K for assuming exclusive carbon/sulfur binary interactions. However, preliminary calculations can still be performed by neglecting the formation carbon/sulfur/hydrogen gaseous compounds and by neglecting carbon/sulfur/hydrogen ternary interactions (as $-S-H$ bonds) on the surface of the crystallites. Preliminary calculations predict that the formation of carbon/sulfur/hydrogen gaseous compounds is very negligible at high temperatures (above 1000 K in the present work). Future work on the carbon/sulfur/hydrogen ternary system will eventually allow more extensive and rigorous calculations.

A second aspect is related to the prediction of the crystallite size growth during heat treatment. No theoretical model exists for the prediction of the evolution of L_a and L_c with temperature for coke crystallites. Nonetheless, an empirical method can be used to approximate the growth of the crystallites during the heat treatment of cokes for a given temperature range.

The carbon/sulfur/hydrogen system will be simplified by considering only the carbon/sulfur and carbon/hydrogen binary interactions correctly predicted by the present coke model. The equilibrium is assumed to consist of coke crystallites with a gaseous phase. The chemical compounds present in the gas phase are $H_2(g)$, $CH_4(g)$, $CS_2(g)$, $CS(g)$, $S_2(g)$, $C_{18}H_{12}(g)$ and $H_2S(g)$. The thermodynamic properties of these compounds are taken from a previous assessment [22, 23].

Concerning the growth of L_c following a given heat treatment, the Equivalent Temperature method will be applied here [38, 39]. The equivalent temperature (T_{eq}) is described as the level of calcination equivalent to that of a given reference green coke following a two hour heat treatment at a given temperature [38]. This method allows the use of (L_c , T_{eq}) pairs which serves as a calibration

curve. If a given coke is heat treated at a given temperature, its Equivalent Temperature (T_{eq}) is determined with the calibration curve. An example of a calibration curve is found [38] and is given by Eq. 2.

$$T_{eq} = 0.0812 \cdot (L_c)^3 - 7.1537 \cdot (L_c)^2 + 225.16 \cdot L_c - 1187.5 \quad (2)$$

Using Eq. 2, at any given T_{eq} , one can calculate a corresponding approximate value for L_c . Assuming $L_c \approx L_a$, for 100g of a given coke containing 96.5 g of carbon and 3.5 g of sulfur, the average L_c value for the coke crystallites is obtained using Eq. 2. Afterward, using FactSage, the model produces the calculation of the predicted thermodynamic equilibrium. The equilibrium sulfur content of the coke crystallites is plotted in Figure 8. Three lines are computed for the addition of 0 g, 1.0 g and 4.0 g of diatomic hydrogen gas ($H_2(g)$) to illustrate the predicted effect of hydrogen. The lower desulfurization temperatures are partially explained by the formation of stable $H_2S(g)$ in the gas phase if some hydrogen is found to be present in the thermodynamic system.

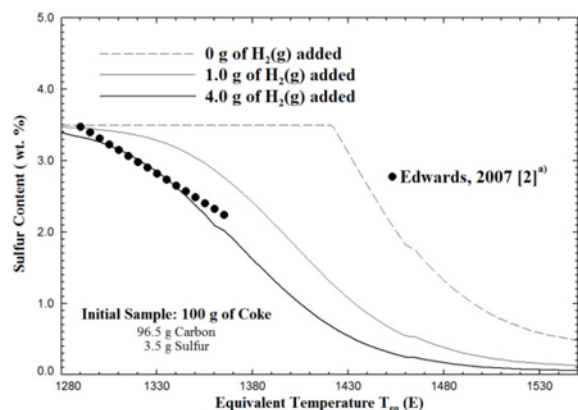


Figure 8. Calculated desulfurization of green cokes using Eq. 2 for the Equivalent Temperature method with addition of $H_2(g)$ ($P_{total} = 1 \text{ atm}$)

a) Measurements reported by [2] for the heat treatment at 1553.15 K of a high sulfur calcined petroleum coke (3.9 wt. % sulfur before heat treatment) placed in the stubholes of anodes baked in an anode baking furnace

In Figure 8, the predicted desulfurization curves are compared to experimental results from Edwards et al. [2]. The Equivalent Temperature calibration curve of [2] is not available. For this reason, Eq. 2 (obtained from [38]) is assumed to be valid for the measurements of Edwards et al. [2]. In their experiment, Edwards et al. measured the evolution of the sulfur content of a high sulfur calcined petroleum coke placed in the stubholes of green anode blocks baked in a Riedhammer furnace at Årdal. It is important to note that the use of stubholes as experimental supports could alter the desulfurization behavior of the studied cokes (i.e. increase the presence of carbon in the studied thermodynamic system during the baking process). Also, assuming that the green anode blocks contain ~16 wt. % pitch and ~84 wt. % calcined coke (and small quantities of recycled anode butts), some hydrogen gas is reasonably assumed to be produced from the heat treatment of the green anodes (typical hydrogen content of ~4.5 wt. % is reported for various pitches [40]). The exact amount of hydrogen exposed to the high sulfur coke is difficult to quantify without further experimental information on the amount of high sulfur calcined

coke used for the desulfurization measurements and the total mass of the green anodes.

In Figure 8, it can be seen that the desulfurization experimental measurements are in agreement with the predictive calculations produced using an initial coke possessing an equivalent amount of 3.5 g of sulfur and 96.5 g of carbon and exposed to 4 g of $H_2(g)$. If one assumes that the heat treatment of the pitch provides this amount of hydrogen during the desulfurization of the studied high sulfur calcined coke, the results in Figure 8 are very relevant.

Conclusion

A new thermodynamic model based on the physical and chemical properties of coke crystallites was presented for the carbon/hydrogen and carbon/sulfur systems. Successful predictions for the desulfurization and dehydrogenation of experimental cokes were demonstrated in this work. A preliminary application of the model to the calcinations of green cokes using the Equivalent Temperature was also discussed. Future improvements of the model will focus on the addition of carbon/sulfur/hydrogen interactions and on the addition of the condensed volatile matter phase to the present coke model. The current model ensures a solid basis for the production of more accurate thermodynamic calculations for the use of carbon in the aluminum industry. If the present thermodynamic model could be combined to a valid kinetic approach, the global model (kinetic + thermodynamic) is expected to provide a better understanding of the combined effects of various industrial parameters (heating rate for example) used for the production of pre-baked anodes.

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