Characterisation of Coke Analogue

Oluwatosin A Aladejebi¹, Brain J Monaghan¹, Mark Reid¹, and Marc in het Panhuis²

¹Engineering Materials Institute and School of Mechanical Materials and Mechatronics, University of Wollongong, Northfield Ave, Wollongong, NSW 2522, Australia
²Soft Materials Group, School of Chemistry and Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, AIM Facility, University of Wollongong, Northfield Ave, Wollongong, NSW 2522, Australia

Keywords: Coke, Coke Reactivity, Coke Carbon, Raman

Industrial coke made from coal, is a complex heterogeneous material, consisting of different carbon types (macerals), inorganic material (minerals) and a highly variable pore structure.¹⁻³ This complexity and heterogeneity make it difficult to isolate specific effects such as mineral type on coke reactivity and carbon structure.

Gill, et al.,⁴ and Niekiek, et al.,⁵ found that the mineral cations present in coke affect its reactivity and could be ranked as follows, $\text{K}_2\text{CO}_3 > \text{Na}_2\text{CO}_3 > \text{CaCO}_3 > \text{MgCO}_3 = \text{MgO} > \text{FeCO}_3 > \text{FeS}_2 > \text{Al}_2\text{O}_3 = \text{SiO}_2$ (little or no change). From the previous works the resulting effect of combination of minerals and porosity on reactivity, and mineral effect on carbon structure were not reported. However, these limitations have the potential to be eliminated or minimised using a coke analogue. Chapman and co-workers⁶,⁷ investigated the dissolution of the analogue in liquid iron and found that the behaviour was similar to those of industrial coke. In addition, Longbottom, et al.,⁸ and Reid, et al.,⁹ investigated the effect of minerals on coke reactivity in $\text{CO}_2$ using the analogue and observed kaolinite, quartz, potash and feldspar reduced the reactivity, as measured by weight loss, whereas lime, gypsum and iron bearing minerals increased reactivity.

In order to fully understand the effect of the mineral phase on the reactivity and carbon structure of the analogue, the porosity of the analogue was first established (using an image analysis technique) to eliminate it as a variable. A pseudo coke reactivity index CRI test similar to the Nippon Steel Corporation method¹⁰ was used to assess the analogue reactivity. Raman analysis technique (Jobin Yvon Horiba 800 Raman spectrum analyser) was employed to characterize the carbon structure of the analogue. Key details of the experiments and findings are given below.

For porosity, the total percentage porosity in the range of 10 – 500 µm for three samples of the analogue and industrial coke are 29 ± 2.3% and 24 ± 4.3% respectively. The standard deviation for the value of coke is likely an underestimate, as it does not adequately represent the inherent variation in a single batch of coke where it is known that there are significant porosity changes in the coke with respect to where the coke was formed (position) in the coke oven. The pore size distribution in the analogue is compared with those of industrial coke, as shown in Figure 1. In the analogue, the pore size is more controlled with less variation than that of the industrial coke.

For reactivity, single minerals with 0.2 mol. of cations per 100g of carbonaceous material after firing were added to the analogue mixture. The relative effects of the minerals were
assessed by reacting it with CO₂ at 1100 °C for 2 hours. The fractional weight change (FWC) of the analogue after reaction was calculated using equation [1], and is presented in Figure 2. The mineral effect on the reactivity of the analogue is ranked from kaolinite to magnetite.

\[ FWC = \frac{\text{mass of reacted analogue} - \text{mass of unreacted analogue}}{\text{mass of unreacted analogue}} \]  

[1]

To assess the carbon structure, approximately 20 optical images of each analogue were obtained and assessed with respect to its optical features to obtain a true representation of the analogue. A typical example is shown in Figure 3(a). The corresponding Raman data are presented in Figure 3(b). The I(D) and I(G) are intensities of the defective and perfect graphitic structures respectively, while the I(V) is the minimum point between the D and G bands.

![Figure 3](image_url)

**Figure 3**: Typical optical image of the base analogue obtained using the Raman optical microscope, showing the textural reflection of the analogue, and (b) Plot showing the carbon structure of the base analogue, where I(D), I(G) and I(V) are key Raman characteristics.

In conclusion, the characterisation of the base coke analogue materials reactivity, porosity and carbon structure with respect to Raman, has been established. The total percentage average porosity is presented in Figure 1.

![Figure 1](image_url)

**Figure 1**: Plot of pore size distribution in (a) coke analogue and (b) industrial coke reproduced from Loison, et al.

![Figure 2](image_url)

**Figure 2**: Plot of Fractional weight change (FWC) in coke analogue with time during its reaction with carbon dioxide gas.
Figure 3: (a) Typical optical image of the base analogue obtained using the Raman optical microscope, showing the textural reflection of the analogue, and (b) Plot showing the carbon structure of the base analogue, where I(D), I(G) and I(V) are key Raman characteristics.

In conclusion, the characterisation of the base coke analogue materials reactivity, porosity and carbon structure with respect to Raman, has been established. The total percentage porosity in the analogue has been shown to be similar to that of industrial coke, and is controllable and reproducible. While its total porosity is similar to that of industrial coke there is less variability with respect to pore size with the majority of the analogues porosity being in the less than 200 µm pore size range.

References
10. ASTM, (D5341-93) Standard test method for measuring coke reactivity index (CRI) and coke strength after reaction (CSR).