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# The Kinetics of the reactivity of a coke analogue with carbon dioxide

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# The Kinetics of the reactivity of a coke analogue with carbon dioxide

## **Abstract**

In this study the suitability of a laboratory analogue for coke for studying the reactivity of coke was evaluated. Coke reactivity and strength are closely related, as such, an improved understanding of the kinetics of blast furnace coke reactions can be used to enhance blast furnace performance. However, coke is a complex composite material, with an inherent heterogeneity with respect to oxide phase composition and phase dispersion. The complexity and heterogeneity of coke makes it difficult to isolate the effects of a specific component on coke reactivity. The coke analogue has been developed to address these issues and was used for controlled testing of specific mineral, and to some degree maceral, effects on reactivity. The reaction of coke analogue with CO<sub>2</sub> was studied using thermogravimetric analysis to measure the kinetics at temperatures from 850 to 1350°C. The reaction rate behaviour of the analogue is similar to that reported for industrial coke. The gasification rate increased with increasing temperature and three reaction zones corresponding to different kinetic control regimes, as found in industrial coke, have been identified. These findings show that the coke analogue demonstrates similar reaction kinetics to industrial coke indicating its suitability for use in coke kinetic studies.

## **Keywords**

analogue, carbon, dioxide, reactivity, kinetics, coke

## **Disciplines**

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# The Kinetics of the Reactivity of a Coke Analogue with Carbon Dioxide

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## Synopsis

In this study the suitability of a laboratory analogue for coke for studying the reactivity of coke was evaluated. Coke reactivity and strength are closely related, as such, an improved understanding of the kinetics of blast furnace coke reactions can be used to enhance blast furnace performance. However, coke is a complex composite material, with an inherent heterogeneity with respect to oxide phase composition and phase dispersion. The complexity and heterogeneity of coke makes it difficult to isolate the effects of a specific component on coke reactivity. The coke analogue has been developed to address these issues and was used for controlled testing of specific mineral, and to some degree maceral, effects on reactivity.

The reaction of coke analogue with CO<sub>2</sub> was studied using thermogravimetric analysis to measure the kinetics at temperatures from 850 to 1350°C. The reaction rate behaviour of the analogue is similar to that reported for industrial coke. The gasification rate increased with increasing temperature and three reaction zones corresponding to different kinetic control regimes, as found in industrial coke, have been identified. These findings show that the coke analogue demonstrates similar reaction kinetics to industrial coke indicating its suitability for use in coke kinetic studies.

## 1 Introduction

Coke plays a key role in the ironmaking blast furnace process. As a fuel, it provides the energy required for the high temperature process. Coke also provides, after reaction with oxygen in the hot blast, the reductant of the iron oxides. Additionally, given that it is the only solid charge material remaining in the lower zone of a blast furnace, coke is a critical material in maintaining the furnace permeability required for the high production rates needed for profitable operation in a modern blast furnace<sup>[1]</sup>.

Coke strength and its resistance to degradation, particularly at high temperatures, are a critical measure of coke quality and predictor of its performance. The hot strength is usually measured using the Coke Strength after Reaction (CSR) test<sup>[2]</sup>. The CSR test measures the effect of coke degradation as a result of reaction with CO<sub>2</sub> gas at 1100°C under standard conditions<sup>[3,4]</sup>. The reaction with CO<sub>2</sub> is given in equation 1, and is known alternately as the Boudouard reaction, the solution loss reaction or the coke gasification reaction. The Coke Reactivity Index (CRI) is a measure of the reactivity of coke with CO<sub>2</sub>, and is generally considered to be inversely proportional to a coke's CSR.

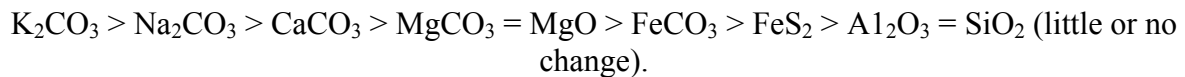


Coal characteristics such as coal rank, ash %, various components in the ash and maceral reflectograms can account for ~70% of the variation seen in the CRI-CSR tests of Australian coals<sup>[2]</sup>. It is difficult to meaningfully characterise what accounts for the other 30%, but it is known that mineral type and ash chemistry in general are implicated<sup>[2]</sup>.

Addressing this last 30% is made difficult due to the nature of coke itself. Coke has inherent complexity, consisting of different maceral and mineral components that, when used at high temperatures, react and interact in such a manner that make isolating the specific component effects on gasification or dissolution difficult. The heterogeneity in coke structure

and spatial distribution of coke minerals, can obscure isolation of specific component impacts. When exposed to high temperatures and reactive atmospheres, the aforementioned compositional and structural features, inherent in a given coke, render isolating the specific component effects on the behavior of a coke difficult.

Several approaches have been used to address the mineral effects on coke reactivity, involving both experimental and statistical studies. The general approach used in the statistical studies was to correlate coke mineralogy with coke reactivity using large industrial data sets <sup>[5-8]</sup>. While these studies did allow some degree of ranking of the relative effect of specific minerals, they produced data of limited accuracy and usefulness when predicting a coke's reactivity. Experimental measurement of the reactivity of cokes made from coals doped with specific minerals prior to coking <sup>[9,10]</sup> found that the effect of mineral cations present in coke could be ranked as follows:



While this work represented a significant improvement in the understanding of key mineral effects on reactivity there were some limitations with the approach, as the ranking was only semi quantitative, not readily translatable to mineral combinations (more than one mineral effect) and did not account for the porosity effects on reactivity or the different carbonaceous types in the coke.

The coke analogue was originally developed for evaluating the effects of minerals on the dissolution behavior of coke in iron <sup>[11,12]</sup>. It is a laboratory-grade material made from graphite, bakelite, novolac and minerals. In the analogue the ash mineralogy, mineral dispersion (distribution within the analogue), particle size and porosity can be controlled to isolate specific effects of the mineralogy on reactivity. In the dissolution studies <sup>[11,12]</sup> it was shown that even though the analogue was made from a mixture that could contain up to around 50% by mass of graphite, its dissolution properties more closely represented that of coke rather than graphite.

In reactivity studies the analogue was reacted with CO<sub>2</sub> in a small scale experiment designed to replicate the CRI test <sup>[13,14]</sup>. In these studies the effects of single minerals and of binary combinations of selected minerals were assessed in terms of their effect on the coke analogue's reactivity. The results of this approach for single mineral additions are given in Figure 1 <sup>[14]</sup>. This figure shows a plot of the effect of added single minerals to the analogue on the reactivity, measured as a fractional weight change (FWC, as defined in equation 2) of the analogue with time. The mineral concentration in the analogues was 0.1 mol. of cations per 100 g of carbonaceous material after firing. This approach allowed clear delineation of the relative effects of the single minerals on the reactivity of the analogue. For binary systems, mixtures of quartz, soda feldspar or troilite with magnetite showed complex reactivity behavior, which was consistent with what might be expected from industrial coke <sup>[14]</sup>.

$$\text{FWC} = \frac{(\text{initial mass}) - (\text{final mass})}{(\text{initial mass})} \quad (2)$$

While it is clear from the reported work on the coke analogue that it can test effects of specific minerals (and perhaps combination of minerals), one key issue associated with the analogue needs addressing: Does the analogue have similar rate-controlling kinetics to that of industrial coke? The main aim of this study is to address this issue. Some preliminary results/findings from this study are presented in this paper.

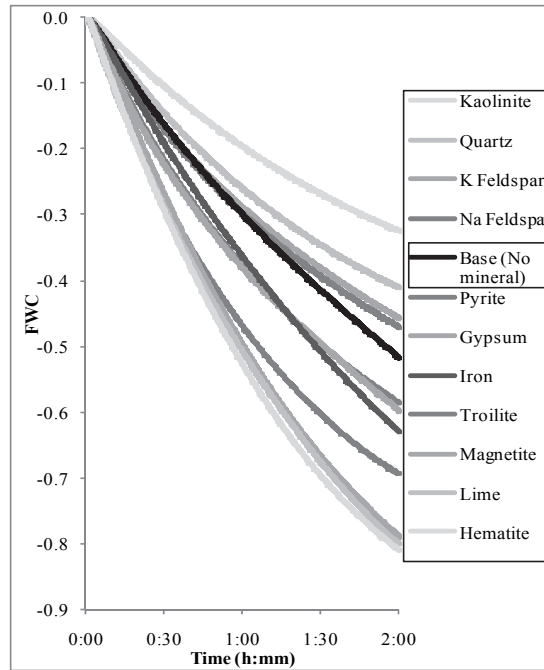


Figure 1. Changes in FWC with time for single mineral-containing coke analogues in CO<sub>2</sub> gas at 1100°C [14]. Note that the legend lists the minerals in their order of reactivity from lowest (top) to highest (bottom). The mineral concentration in the analogues was 0.1 mol. of cations per 100 g of carbonaceous material after firing.

## 2 Experimental

### 2.1 Making the Coke Analogue

The coke analogue is an extruded cylinder manufactured from mixtures of graphite and phenolic resin that is then fired in an argon atmosphere at 1200°C. The stepwise firing procedure involved curing at 170°C for 24 hours, heating to 950°C and holding for one hour then cooling to 50°C at 5°/min. It is then heated again to 1200°C and held for one hour and then cooled to 50°C at 5°/min. The proportions of the different components used in the preparation of the coke analogue samples are given in Table 1. The preparation procedure results in an analogue of cylindrical shape, nominally 8 g in mass, 18 mm in diameter and 30 mm in height. After firing, the analogue was sectioned, mounted in resin and prepared for optical and electro optical analysis and Raman spectroscopy. All samples were polished to a 0.25 µm finish and SEM samples were carbon coated.

Table 1. Components used to produce coke analogue

Material	Purity	Size	Addition	Primary Function(s)
Graphite Powder 1	99.99+%	< 45µm	28% of dry base	Carbon source
Graphite Powder 2	99.99+%	< 150µm	28% of dry base	Carbon source
Phenolic resin (Bakelite)	N/A	+100µm -250µm	44% of dry base	Porosity control
Liquid 45% Novolac Resin in propylene glycol	N/A		Ratio of 0.52 liquid / dry mix	Binder Porosity control
hexamethylenetetramine (HTMA)	N/A		3mass% of liquid resin	Curing agent

## 2.2 Reactivity Tests

Reactivity tests were carried out in a thermogravimetric analysis (TGA) system, used to log the temperature and weight loss of the sample during the experiment with time. In the TGA experiments coke analogue samples were reacted with carbon dioxide, at constant temperature. A schematic of the experimental set up is shown in Figure 2.

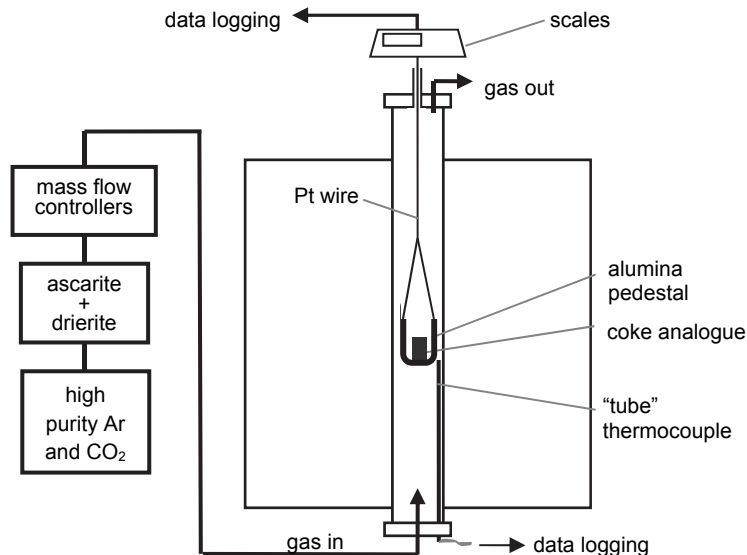


Figure 2. Schematic of the TGA set up used for the coke analogue reactivity testing.

The coke analogue samples were heated at 10°C/min under high purity argon to temperatures in the range 900-1350°C. The argon flow rate was 1 L/min. The samples were held inside an alumina pedestal to allow the access and exit of gas. At the reaction temperature, the gas was changed from argon to carbon dioxide, flowing at 4.5 L/min. The sample was held under these conditions for 120 minutes, after which the gas was changed back to argon, and the furnace cooled.

## 3 Results and Discussion

A coke analogue with no minerals was reacted isothermally with CO<sub>2</sub> at temperatures between 900°C and 1350°C, with a step size of 25°C.

The rate of reaction ( $R_C$ ) was calculated from the logged weight change data using equation 1,

$$R_C = -\frac{1}{W_o} \frac{dW}{dt} \quad (1)$$

where  $W$  is the weight of the sample,  $W_o$  the initial weight of the sample and  $t$  time. The relation between the reaction rate and temperature was investigated using an Arrhenius plot ( $\ln R_c$  against  $1/T$ ), shown in Figure 3. Three separate temperature regions with a linear relation between  $\ln R_c$  and  $1/T$  were identified. These regions correspond to those identified by Walker *et al.* [15] and Szekely *et al.* [16] for carbon gasification, and correlate to different kinetic control regimes. The three regions are:

Region I – Chemical reaction controlled region

Region II – Chemical reaction + pore diffusion controlled region

Region III – Mass transport controlled region

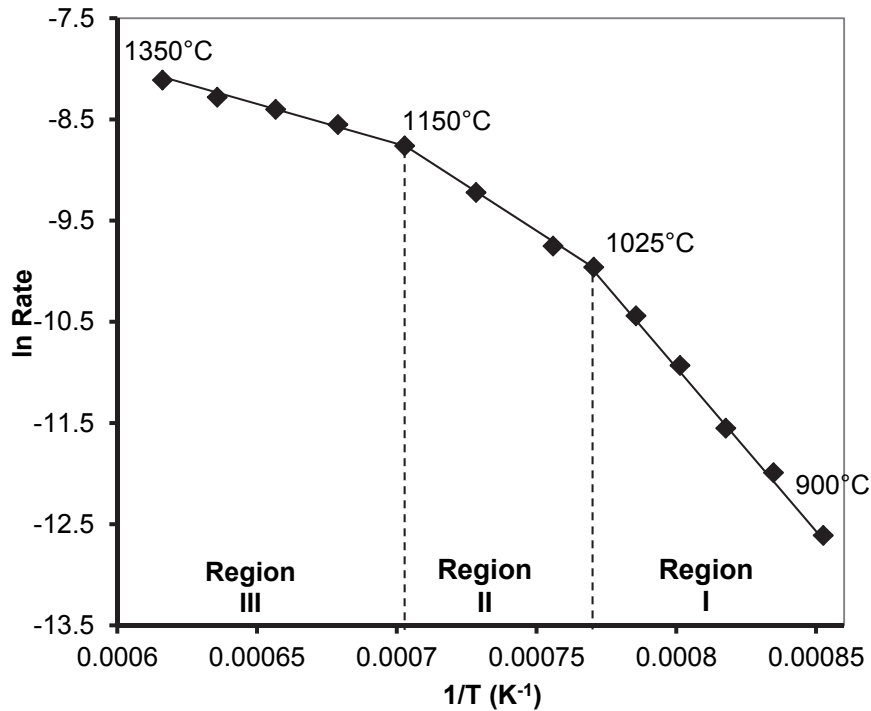


Figure 3. Arrhenius plot of ln Rate against 1/T for the coke analogue with no added minerals reacting with CO<sub>2</sub> at 4.5 L/min.

The temperature ranges given in the literature for the different regions for different carbonaceous materials are given in Table 2. The temperature ranges found for the coke analogue with no mineral matter fit largely within those reported in the literature. However, the ranges given for the different regions for the different carbonaceous materials vary greatly.

Table 2. Temperature ranges for regions I, II and III for different carbonaceous materials.

Reference	Material	Region I	Region II	Region III
Current results	coke analogue	900-1025°C	1025-1150°C	>1150°C
Turkdogan and Vinters <sup>[17]</sup>	graphite	up to 800-900°C	1000-1300°C	–
Jess <sup>[18]</sup>	activated carbon	467-560°C	–	>688°C
Liu <i>et al.</i> <sup>[19]</sup>	char	< 1176°C	>1176°C	–
Grigore <sup>[20]</sup>	cokes	up to 870-931°C	–	–
Wicke <sup>[21]</sup>	coke	900-1200°C	–	–
Irfan <i>et al.</i> <sup>[22]</sup>	coal	< 1200°C	–	–

Much of the published work on CO<sub>2</sub> reactivity with coke has been carried out in the low temperature range (850 to 1150°C, region I) where chemical reaction controls the rate, although higher temperature and associated reactions mechanisms also have relevance when considering coke reactivity in the blast furnace. Due to the relative abundance of data in this low temperature region, a better comparison for the current results could be against the reaction rates reported for region I.

The measured rates of reaction from the low temperature region (region I) are compared against the literature<sup>[20,23-25]</sup> in Figure 4. Figure 4 shows that the industrial cokes and the coke analogue (with no mineral matter) largely display similar reaction behaviour. It may also be seen that the coke analogue had, in general, a lower reaction rate than those reported for the industrial cokes. The number of active carbon sites affects the rate of reaction<sup>[15]</sup>. Further, the formation of these carbon active sites is known to be related to minerals, maceral size and type and micro-texture of the coke. Subsequently, these factors all

affect the reactivity of coke. The coke analogue has a more controlled but finer pore structure and lower overall porosity than is generally found in industrial cokes. This is a possible reason for the lower reaction rates for the analogue in Figure 4.

In addition, the coke analogue examined in the testing to date has contained no mineral content. It is well known that the presence of minerals in cokes can increase or decrease the reactivity of cokes [5,7-10]. This is also true for the coke analogue [13,14]. As shown in Figure 1, the addition of certain (Fe- and Ca-containing) minerals to the coke analogue has increased the rate of reaction of the coke analogue at 1100°C. Thus the addition of minerals to the coke analogue may increase the reaction rate such that it more closely agrees with the results for the industrial cokes. Further study in this project will focus on the effect of selected minerals on the kinetics of the coke analogue reactivity.

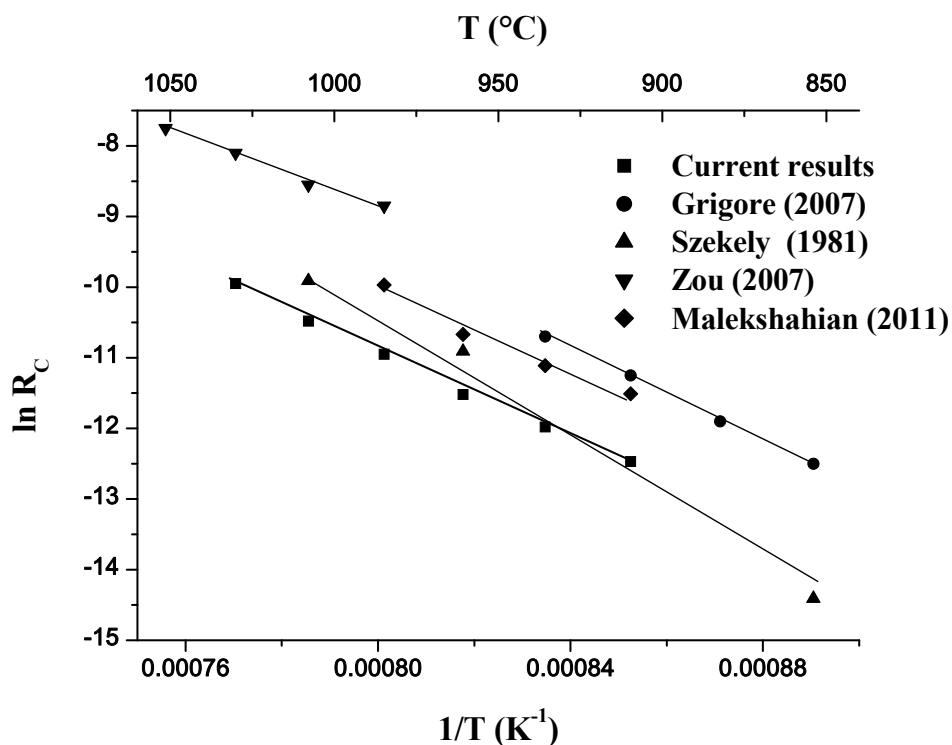


Figure 4. Comparison of the current results with previous studies [20,23-25].

#### 4 Conclusions

A coke analogue with no added mineral matter has been reacted with carbon dioxide at different temperatures between 900 and 1350°C to investigate the kinetics of the reaction. For the coke analogue three temperature regions corresponding to chemical reaction control, chemical reaction and pore diffusion control, and mass transfer control, were identified based on the rate controlling mechanisms as previously observed for coke gasification studies.

The reactivity of the coke analogue was close to, but generally lower than that for industrial cokes in the literature. The lower reactivity of the coke analogue could be explained by the absence of minerals in the analogue examined, or by the finer and lower total porosity of the coke analogue. However, the similarities in the behaviour of the coke analogue and industrial cokes indicate that the coke analogue can be a suitable laboratory tool for the further study of coke gasification kinetics.

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