

Effect of Mineral Matter on the Reactivity of Coke and its Replication in a Coke Analogue

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The reactivity of coke analogues doped with minerals to mimic the mineralogy of specific industrial cokes was compared with the reactivity of the industrial cokes. The reactivity was assessed in a pseudo-CRI type test. This involved reacting the carbonaceous materials (analogue and industrial coke) in CO₂ at 1 100°C in a thermos-gravimetric system. In this comparison, the mineral matter added to the coke analogue was prepared from ashing of the industrial cokes. A distinct ranking of reactivity for the industrial cokes was determined to be coke A < coke B < coke C. The high reactivity of coke C was attributed to the high iron content in its ash. The higher reactivity of coke B over coke A was attributed to its higher porosity and lower rank (of the original coal carbon type) of the industrial cokes. The coke analogue replicated the increased reactivity of coke C over cokes A and B, indicating that the coke analogue is able to some extent to replicate the effect of coke mineralogy on coke reactivity in CO₂. The use of the coke analogue allowed assessment of the difference in the reactivities of cokes A and B. When porosity and carbon type were fixed by use of the analogue, the reactivities of the analogues of cokes A and B were found to be similar.

KEY WORDS: metallurgical coke; coke analogue; reactivity; CRI; minerals.

1. Introduction

Coke is a key material in blast furnace ironmaking, with its properties having a direct effect on the quality and productivity of the ironmaking process.¹⁾ It is fuel for the furnace, the carbon source for the CO reductant of iron oxide and provides the structural support for the blast furnace burden. The performance of coke in the blast furnace is related to its hot strength and reactivity.^{2,3)}

It is desirable to predict the reactivity of coke from its key characteristics. Unfortunately this is in part limited by unknown or non-quantified effects of minerals on coke reactivity. Elucidation of the effects of minerals on coke reactivity has proved difficult due to its complexity, being comprised of different forms of carbonaceous materials (macerals), mineral components and pore structure dependent on the volatile matter in the source coal (and coking conditions).^{2,4,5)} Coke also has significant heterogeneity in any metric(s) used to characterise its maceral grouping, mineralogy, phase dispersion, morphology and porosity. When exposed to high temperatures and reactive atmospheres,

these compositional and structural features, inherent in a given coke, render isolating the specific component effects on the behaviour of a coke difficult.

A coke analogue has been developed as a tool to aid quantitative assessment of the effects of minerals and porosity on coke reactivity. The analogue is made from a number of carbonaceous materials and can be doped with minerals, including those simulating industrial coke mineralogy and porosity. The coke analogue has been used to study the effect of specific minerals and mineral combinations on coke reactivity with CO₂ at high temperatures,^{4,6)} to assess the reaction rate controlling mechanisms of the analogue gasification⁷⁾ and to mimic the behaviour of industrial coke on dissolution in liquid iron.^{8–11)} In a previous investigation on the effects of minerals on the reactivity of coke by coke analogue method,⁴⁾ single minerals were added to the coke analogue at a concentration of 0.1 mol cations per 100 g of base coke analogue, and it was found that their relative effect of the rate of reaction, as expressed in the weight change of the sample over two hours, was hematite > lime > magnetite > troilite > gypsum > pyrite > base analogue (no mineral) > Na Feldspar > K feldspar > quartz > kaolinite. These relative reactivities were consistent with those expected for mineral reactivity effects in industrial

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coke. In the rate controlling mechanism study of analogue gasification, over the temperature range 900°C to 1350°C, the reaction mechanism for the gasification was found to be consistent and similar to that reported for industrial coke.⁷⁾

In the analogue dissolution study, an analogue was built to replicate (mimic) a specific industrial coke’s mineralogy and then its dissolution behaviour in iron was compared with the industrial coke. It was found that dissolution behaviour of the analogue was similar to that of the industrial coke the analogue was built to mimic.^{8–11)} A comparable approach towards coke gasification in CO₂ has not yet been performed and is what is reported in this article.

The aim of this study was to develop coke analogues doped with minerals to mimic the mineralogy of specific industrial cokes and assess and compare their gasification reactivity with the industrial coke.

2. Experimental

The experimental concept for this work was to test the reactivity of industrial cokes with carbon dioxide in a thermogravimetric analysis (TGA) system, a pseudo-CRI test. The pseudo-CRI test was designed to reflect the conditions in a standard CRI measurement.¹²⁾ The reactivities of industrial cokes were then compared with those for coke analogues containing the same minerals. The minerals for the coke analogues were prepared by ashing the industrial cokes. Characterisation of both the industrial cokes and coke analogues allowed key physical properties of both the industrial cokes and coke analogues to be taken into account.

2.1. TGA Reactivity Test

A TGA system, as shown in Fig. 1, was used to measure the reactivity of the carbonaceous materials in a CO₂ atmosphere at 1100°C. The sample, of a nominal 8 g, was weighed and then placed in an alumina crucible hung from a balance. The system was heated at 10°C/min to 1100°C under Ar flowing at 1 L/min. The gas was then switched to CO₂ at 2 L/min flow rate. After 2 hours, the CO₂ was

switched off and the sample cooled down under Ar. The gases used were high purity (99.99%) and further purified by passing through drierite and ascarite prior to entering the furnace. The Ar was further cleaned by passing it through Cu turnings at 300°C.

The fractional weight change (FWC) was used to characterise the extent of gasification and was calculated using Eq. (1),

$$FWC = (W - W_0) / W_0 \dots \dots \dots (1)$$

where W₀ and W are the initial mass and the mass of a sample at time t, respectively, g.

2.2. Materials

Cokes A to C were obtained from Australian industry. Samples of coke A for the TGA test were prepared by cutting lumps into a rough cylinder with a nominal weight of 8 g. Cokes B and C were supplied in the form of CRI lumps (crushed and sieved to 19–21 mm), consequently 7 to 8 pieces were used to make up the 8 g used for the TGA reactivity test. The ash analysis, porosity and coal rank (as given by mean reflectance) for each industrial coke are presented in Table 1.

The coke analogue was prepared from a mixture of graphite, Novolac resin, Bakelite and hexamethylenetetramine (HTMA). Full details of the preparation have been given elsewhere.^{6,7)} This method produces analogue samples of cylindrical shape of ~8 g in mass, 18 mm in diameter and 30 mm in height.

The mineral matter for the coke analogue was prepared

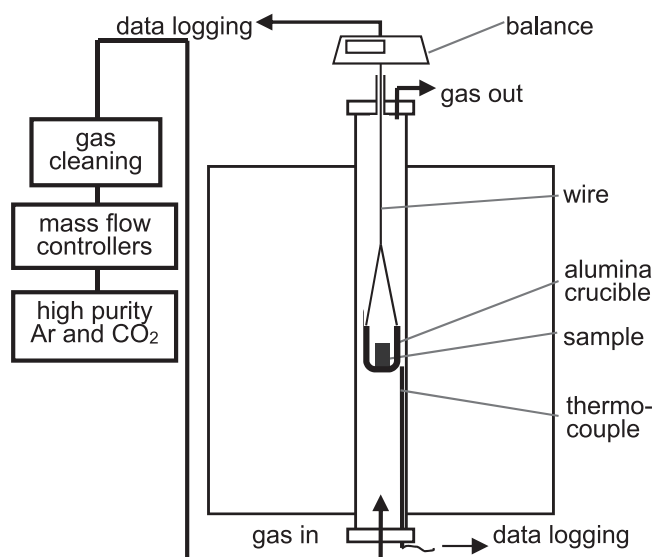


Fig. 1. Schematic diagram of the TGA system used for the reactivity test.

Table 1. Properties of the coke samples.

Sample	Coke A	Coke B	Coke C
Rank as given by mean reflectance, R _o	1.13	0.90	1.09
Porosity (vol%)	37.8	48.4	34.6
Ash content (%db)	12.6	11.2	11.3
Ash analysis (XRF, mass%)			
SiO ₂	55.7	50.8	53.8
Al ₂ O ₃	29.7	38.3	27.4
Fe ₂ O ₃	6.60	4.56	9.00
CaO	2.07	1.21	2.65
MgO	0.72	0.54	1.14
Na ₂ O	0.49	0.39	0.33
K ₂ O	1.06	0.74	1.61
TiO ₂	1.35	1.90	1.40
Mn ₃ O ₄	0.09	0.04	0.10
SO ₃	0.35	0.08	0.53
P ₂ O ₅	1.03	0.69	1.30
SrO	0.07	0.07	0.08
BaO	0.08	0.06	0.07
ZnO	0.03	0.04	0.02
V ₂ O ₅	0.04	0.08	0.05

by ashing the industrial cokes. Each industrial coke was crushed to -2 mm. Approximately 100 g of a coke sample was placed in an alumina tray and placed in a muffle furnace at 520°C in air. The sample was stirred daily to help expose the entire sample to the air. The ashing was continued for one week, or until the rate of weight change of the sample was less than 0.1 g/day. The ash from each of the industrial cokes was characterised by XRD.

The ash from each industrial coke was added to the coke analogue at a constant proportion of 10 mass%. The ash was ground to $38\ \mu\text{m}$ before addition to the analogue. The morphology and distribution of the mineral matter in both the industrial cokes and coke analogues were characterised by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis.

3. Results/Discussion

3.1. Reactivity of Industrial Cokes and Coke Analogues

The FWC curves for the gasification of the industrial coke samples with CO_2 at $1\ 100^{\circ}\text{C}$ are shown in Fig. 2. The reactivity test for coke A was repeated three times, while cokes B and C were each tested twice, with each repeat represented by a curve in Fig. 2. The three industrial cokes have very different reactivities. Ranking the cokes from least reactive to most reactive, coke A < coke B < coke C. These reactivities measured by the TGA test are in the same order as the CRI values (Table 2).

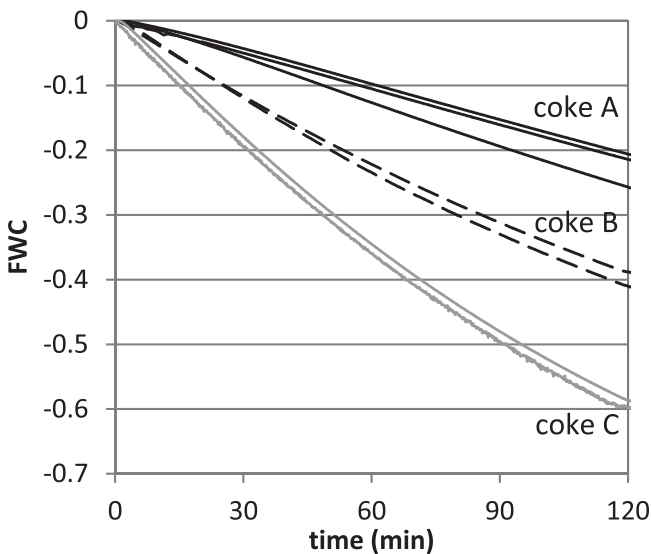


Fig. 2. FWC curves for the reaction of the three industrial cokes with CO_2 at $1\ 100^{\circ}\text{C}$.

Table 2. CRI and FWC at 60 and 120 minutes for the industrial coke samples and coke analogues containing coke ash.

	Industrial coke			Coke analogue	
	CRI (%)	FWC 60 min	FWC 120 min	FWC 60 min	FWC 120 min
Coke A	19.4	0.110	0.230	0.281	0.466
Coke B	30.4	0.228	0.396	0.290	0.449
Coke C	38.0	0.353	0.595	0.346	0.551

The reactivities of coke analogues containing 10 mass% of ash from the industrial cokes, ground to $-38\ \mu\text{m}$, were also measured in the TGA. The FWC curves for the coke analogues with ground industrial coke ash during reaction with CO_2 at $1\ 100^{\circ}\text{C}$ are given in Fig. 3.

Table 2 summarises the FWC values at 60 and 120 minutes for the industrial cokes and the coke analogues containing coke ash. The trends in the reactivities of the coke analogue samples are different from those of the industrial cokes. For the industrial cokes, there was clear delineation between coke A (least reactive), coke B (intermediate) and coke C (most reactive). With the coke analogues, there was clear delineation between the analogues with ash from coke C (most reactive) and analogues with ash from cokes A and B (approximately equally least reactive). Why the coke analogue containing the coke ash had a different trend to the industrial cokes raises two key questions.

The initial question is whether or not the TGA methodology for measuring the reactivity was suitable. The results in Table 2 show that for the industrial coke samples the CRI values and the measured FWCs showed similar rankings between the cokes. This agreement with respect to reactivity of both the CRI and TGA testing is supportive of the TGA test methodology being suitable for the industrial cokes.

The second question is whether the coke analogue is a suitable tool for examining the reactivity of cokes. The coke analogue appears to be discriminating to some extent, with coke C being the most reactive in both the coke and the analogue. If the coke analogue is a suitable tool for examining the reactivity of cokes, the causes of the difference in the trends seen in the industrial coke samples and the coke analogues need to be further examined.

It is known that a number of factors affect the reactivity of coke.^{13,14} Among them, ash composition and mineralogy, porosity and carbon type are most relevant to the current investigation. Each of these factors are discussed in turn. Given resource constraints it was not possible to fully address/separate coal rank and porosity effects in the approach used as porosity and effective rank are ostensibly

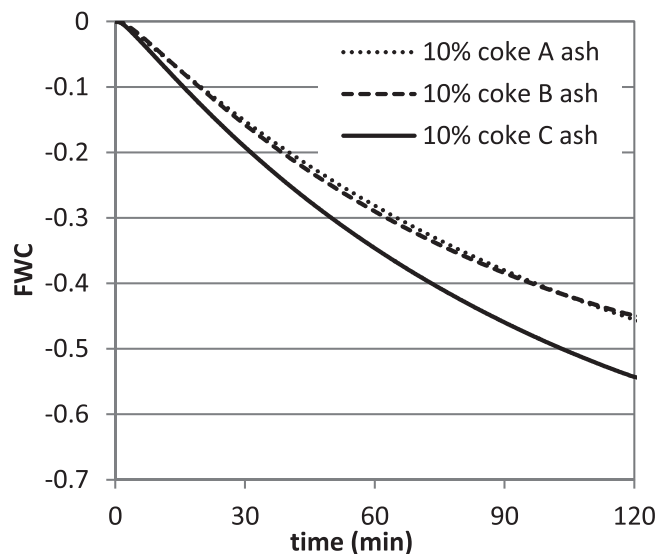


Fig. 3. FWC curves for the reaction of coke analogues containing 10 mass% industrial coke ash ground to $-38\ \mu\text{m}$ with CO_2 at $1\ 100^{\circ}\text{C}$.

constant in the analogue. In spite of this constraint much of their effects, under the conditions studied, can still be inferred or understood in comparison of the reactivates of the analogues with the industrial coke.

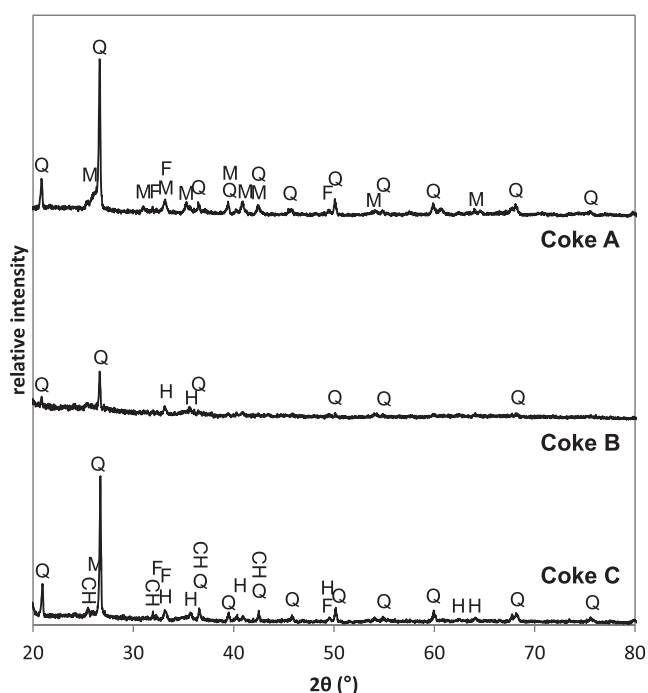
3.2. Ash Mineralogy and Composition

Coke mineralogy is known to have a large effect on coke reactivity. Some minerals are known to increase the reactivity of a coke, while others decrease the reactivity.^{4,15)}

Reid *et al.*⁴⁾ investigated the relative effects of single metals/minerals on the reactivity of coke analogue. Among the listed ash components listed in Table 1, Fe_2O_3 , CaO , MgO and the alkalis increase the reactivity of cokes.^{4,15)} Summation of these components gives 10.9 mass% in coke A, 7.4% in coke B and 14.7% in coke C. From the simple summation of these components, it would be expected that both industrial cokes and corresponding analogues should have a reactivity sequence of coke B < coke A < coke C. However, this was not the case. Other ash components are expected to decrease the reactivity. However, their effects, and the differences in contents of these between the cokes, are much smaller compared with those components that increase the reactivity.

A better measure of the coke ash is their mineralogy. The XRD patterns of the resulting ashes are presented in Fig. 4. Quartz appears as the major crystalline phase in each case. Apart from this, the mineralogy of the coke ashes is quite different. The ash from coke A was found to mainly contain quartz and mullite, with a small amount of fluorapatite. The ash from coke B appeared to have a high amorphous content besides quartz and hematite. The coke C ash contained quartz, hematite, fluorapatite and chamosite.

Microstructural analysis of the mineral matter within



M – mullite ($\text{Al}_6\text{Si}_2\text{O}_{10}$), Q – quartz (SiO_2), F – fluorapatite ($\text{Ca}_5\text{F}(\text{PO}_4)_3$)
CH – chamosite ($(\text{Fe}^{2+}, \text{Mg})_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$), H – hematite (Fe_2O_3)

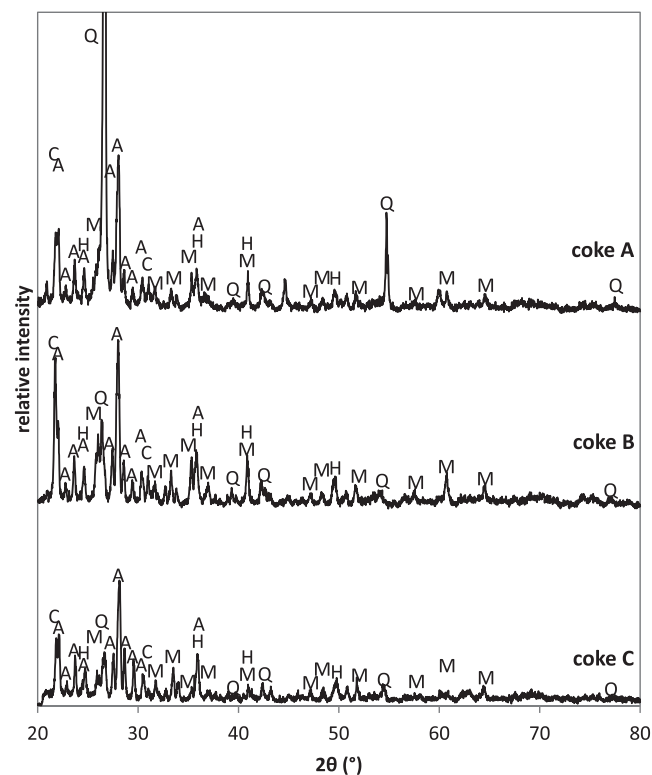
Fig. 4. XRD patterns of the ashes produced from cokes A, B and C at 520°C.

the industrial cokes by SEM and EDS was conducted. Due to space restrictions the micrographs are not shown here, however a summary of what was found follows. Aluminosilicates were the major mineral species in each industrial coke. Some key differences were noted in the distribution and composition of the minerals in the cokes. There were differences in the abundance of Fe-bearing minerals, with coke C containing the most (as expected from the ash composition, Table 1), with coke A containing less and coke B the least.

From the minerals identified within each of the ashes (Fig. 4), it is expected that coke C has the highest reactivity, but it is difficult to estimate the relative reactivities of cokes A and B due to the highly amorphous nature of the coke B ash.

The mineralogy of the ashes of reacted coke analogues was also examined by XRD (Fig. 5). The mineral matter remaining after reaction from the analogues of cokes A and C was generally similar to their respective starting industrial coke ash, with some formation of anorthite. The amorphous aluminosilicate components in the original coke B ash crystallised during coking (at 1 200°C for 60 minutes) and reaction (at 1 100°C for 6 hours), resulting in a XRD pattern similar to that of coke A except for its significantly lower quartz content. These changes in the mineral matter of coke B during the reaction are unlikely to account for the difference in reactivity seen between the industrial cokes and the coke analogues.

The difference in the mineralogy of the cokes likely explains the increased reactivity of coke C over cokes A and B. From the composition of the minerals in coke C it would



Q – quartz (SiO_2), M – mullite ($\text{Al}_6\text{Si}_2\text{O}_{10}$), A – anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)
H – hematite (Fe_2O_3), C – cristobalite (SiO_2)

Fig. 5. XRD patterns of the remnant oxide components in coke analogues after reaction with CO_2 at 1 100°C for 6 hours.

be expected to have the highest reactivity of the cokes. Replication of this in the coke analogue indicates that the coke analogue can be used to show the effect of complex mineral combinations on reactivity.

However, only considering the mineralogy of the cokes does not fully explain the reactivities of the different industrial cokes, and cannot explain all the differences between the industrial cokes and the coke analogues containing ash.

3.3. Porosity

The mineralogy (both composition and particle size) of the cokes could not fully explain the difference in the trends in the reactivity between industrial coke and the coke analogues containing ash. Other obvious differences between the cokes were the porosity of the samples (Table 3).

The porosity of coke has a large effect on the reactivity, with an increase in the porosity of coke leading to an increase in its reactivity. A general rate equation for a heterogeneous reaction could be written in the form of Eq. (2).^{7,16)}

$$d(FWC)/dt = k A \Delta C^n \dots\dots\dots (2)$$

From this equation we can see the rate of reaction is a function of reaction rate constant *k*, *A* the contact area for the reactions and ΔC a gas concentration change that can be approximated to the thermodynamic driving force for the reaction.⁷⁾ The specific or appropriate values for *k*, *A* and ΔC in Eq. (2) are dependent on the prevailing rate controlling mechanism, which varies with temperature. The area term under consideration here would be that of the carbon and CO₂ gas. The reaction rate (reactivity) is directly proportional to the contact area *A*, and the contact area being a function of porosity. Given this, it is expected that the reaction rate is strongly related to porosity.

The porosity of the industrial cokes was given in Table 1, while the porosity of the coke analogue samples is given in Table 3. Coke B had a much higher porosity than the other industrial cokes. This may then account for the relative high reactivity of coke B in comparison to coke A. In contrast to the industrial coke samples, the analogues containing the ash from cokes A and B have similar porosities. This may well partially explain the difference in the relative reactivities of the industrial cokes and the coke analogues containing the ash of cokes A and B.

The porosity of the analogue with coke C ash was slightly higher than those for the other two analogues. Minerals with a high Fe content can cause an increase in the porosity of these samples, likely caused by the reduction of iron oxides during coking, which consumes carbon and forms gas, both of which increased porosity. This expected increase in

porosity also contributed to the increase of the reactivity. Thus, it is likely that the higher reactivity of the analogue containing coke C ash is caused both by an increase in porosity and by its mineralogy.

The difference in the relative reactivities of cokes A and B for the industrial coke samples and coke analogues is at least in part due to the differences in the porosity of the industrial cokes, which is (by design) not present in the coke analogue samples.

When the porosity effects are removed by the use of the coke analogue the mineral effects dominate. Consequently, cokes A and B have similar reactivities, while coke C had a higher reactivity.

3.4. Rank

The carbon types present in the industrial cokes can have a large effect on the reactivity. Coal rank is known to be strongly related to the rank of the parent coals used to produce the coke. Cokes A and C came from coals with similar rank, as indicated by the reflectance given in Table 1. On the other hand coke B came from a lower ranked coal. In general, lower ranked coals form cokes with higher reactivities.^{2,16)} Focusing on rank, assuming all other factors being equal it would be expected that cokes A and C have a similar reactivity and coke B having a higher reactivity. Difference in the carbon type in the industrial coke samples are specifically not replicated in the analogue. This may in part explain the similar reactivity of analogues with coke A and coke B ash.

It is likely that the difference in the trends in reactivity seen between the industrial cokes and the coke analogues with industrial coke ash are to some degree due to differences in the carbon types between the industrial cokes. These differences are at least in part nullified within the coke analogue, so different relative reactivities between samples are expected.

When the carbon type/rank effects are removed by the use of the coke analogue the mineral effects dominate. Consequently, the analogues of cokes A and B have similar reactivities, while coke C had a higher reactivity.

3.5. Possibilities of Use of the Coke Analogue for Coke Reactivity Studies

While the study of coke reactivity in CO₂ is complex and results difficult to interpret, from the results presented in this study, the coke analogue demonstrated its use in separating effects of carbon type and porosity on reactivity allowing evaluation of specific mineral effects. Though it is recognised there is still much work to fully understand coke reactivity, particularly the effects of particle size, mineral phase and porosity of the analogue on reactivity, the results presented go some way to validating the analogue for sue in such an endeavour.

4. Conclusions

The reactivity of the industrial cokes in CO₂ gas was in the sequence of coke A < coke B < coke C. The high reactivity of coke C was attributed to its mineralogy, especially the high iron oxides content. The higher reactivity of coke B over coke A is thought to be due to its higher porosity

Table 3. Porosities of coke analogue samples containing 10% industrial coke ash ground to -38 μm, measured by mercury porosimetry.

	porosity (%)
Coke A	38.75
Coke B	39.19
Coke C	43.27

and the lower rank of original coal carbon type/rank effects in the industrial cokes.

From a mineral effect on reactivity perspective the coke analogue replicated the increased reactivity of coke C over cokes A and B. This indicates that the coke analogue is able to some extent to replicate the effect of coke mineralogy on coke reactivity in CO₂.

The use of the coke analogue allowed assessment of the difference in the reactivities of cokes A and B. When the effects of both porosity and carbon type were fixed (removed) by use of the analogue, the reactivities of the analogues of cokes A and B were similar.

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