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DEVELOPMENT OF A METALLURGICAL COKE ANALOGUE TO INVESTIGATE THE EFFECTS OF COKE MINERALOGY ON COKE REACTIVITY

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Abstract

In this study the suitability of a laboratory analogue for coke for studying the effects of minerals on the reactivity of coke was evaluated. In addition to this, the effects of different physical properties and production conditions on the reactivity of the coke analogue were also tested. The coke analogue was used for control testing of specific mineral, and to some degree maceral, effects on reactivity. Such information would improve our fundamental understanding of coke reactivity behaviour and could be used to develop more accurate predictive models of coke strength after reaction (CSR) or associated indices and coke properties.

The effect on reactivity of the addition of different simple minerals to the coke analogue was evaluated by conducting pseudo-coke reactivity index (CRI) tests. It was found that the addition of minerals to the coke analogue had an effect on its reactivity. While the addition of minerals also affected physical properties such as porosity, it was found that the minerals themselves played a role in determining the reactivity of the coke analogue. The principal conclusion of this study though is that the coke analogue has been identified as having potential to be a suitable tool for studying the effects of mineralogy on coke reactivity in a CSR/CRI like test.

1 Introduction

Coke strength and its resistance to degradation, particularly at high temperatures, are a critical measure of coke quality and predictor of its performance. One property of coke which plays a vital role in determining its hot strength is its mineralogy [1]. Progress in the area of assessing the impact of minerals on coke strength has been limited by:

- The inherent complexity of coke. Coke is made up 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, which obscures isolation of specific component impacts.

As a result there are still a number of unresolved questions relating to coke's high temperature characteristics, reactivity and strength [2,3].

The hot strength is usually measured using the Coke Strength after Reaction (CSR) test. The CSR test measures the effect of coke degradation as a result of reaction with CO_2 gas at 1100°C under standard conditions [4,5]. The Coke Reactivity Index (CRI) is a measure of the reactivity of coke with CO_2, and is generally considered to be inversely proportional to a coke's CSR.

A material, called coke analogue, has been developed for use as a tool in laboratory scale research into the properties of coke. The analogue was originally developed to mimic the dissolution behaviour of coke in liquid iron but is now being used in the study of coke mineral reactivity at high temperature [6,7,8,9]. The analogue is made from a number of carbonaceous materials and can be doped with minerals to simulate an industrial coke's mineralogy. In addition to being able to simulate the mineralogy of the coke, the coke analogue offers the advantages of having control over the porosity, carbon structures and mineral dispersion through the coke. Further, the analogue can be formed into simple shapes that allow its strength to be measured in standard compression strength techniques. These advantages should lessen and in some cases eliminate the heterogeneity problems normally experienced in coke laboratory studies and allow the testing of specific minerals and mineral combinations on the coke reactivity and strength.

The aim of this study is to understand the specific mineral effects on the properties and reactivity of coke. To this end, different minerals, in different amounts were added to the coke analogue and tested under conditions analogous to the CSR/CRI tests.

2 Experimental

2.1 Coke Analogue Preparation

Coke analogue samples were prepared from mixtures of differently sized graphite particles and phenolic resin and fired at temperatures up to 1600°C. The proportions of the different components used in the preparation of the coke analogue samples are given in Table 1. Details of the preparation of the coke analogue were given in Monaghan *et al*. [7,8] and Longbottom *et al*. [9]. The choice of firing temperature was based on work focused on coke dissolution in iron and not to represent coke making temperatures [3]. A set of standard conditions were chosen to represent a baseline material, against which the behaviour of the other samples could be compared against. These were a coke analogue sample containing no mineral matter, fired to 1600°C. These conditions were chosen as they represent a simple baseline material easy to characterise and describe, and that extant data on this base material

[7-9] combined with future measurements will allow in-depth analysis and long term batch variability testing.

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		3 mass% of liquid resin	Curing agent
Non carbonaceous materials	N/A	As required	As required	Mineral matter
Dry base consists of graphite and Bakelite powder. Dry mix included dry base and any non-carbonaceous materials added.				

Several variables were tested during this project by the production of different coke analogue samples. The bulk of these samples were produced with different types and amounts of mineral matter, including silica in different phase structures (quartz and cristobalite), sodium added as sodium carbonate, and magnesia. The effect of the particle size of the quartz addition was also investigated. The amount of minerals added was calculated and is reported in terms of moles of metal (cations) added per 100g of the total mass. Mineral additions to the coke analogue were prepared by grinding to -38 µm. The coarse quartz was prepared by sieving coarse sized quartz to -150 +125 µm.

2.2 Reactivity Tests

Pseudo-CRI tests were carried out in a thermogravimetric analysis (TGA) system. In a TGA, the temperature and weight loss of the sample during the experiment are logged with time. The conditions used were principally based on the standards ASTM D5341 [4] and ISO 18894 [5] for reactivity measurement of industrial cokes. In the TGA experiments coke analogue samples were reacted with carbon dioxide, at constant temperature of 1100°C. A schematic of the experimental set up is shown in Figure 1.
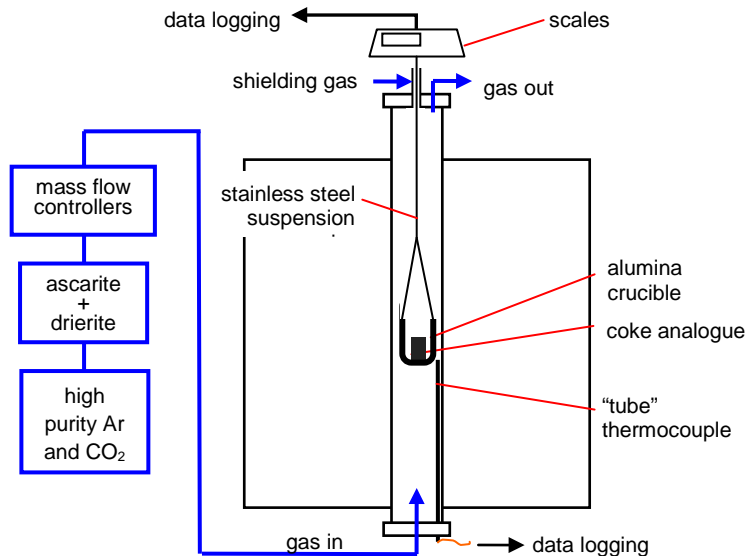

Figure 1. Schematic of the TGA set up used for the coke analogue reactivity testing.

The coke analogue samples were heated at 20°C/min under high purity argon. The argon flow rate was 1L/min. The samples were held inside an alumina crucible that had holes machined into the sides (~4mm in diameter) to allow the access and exit of gas. At 1100°C, the gas was changed from argon to carbon dioxide, flowing at 2L/min. The sample was held under these conditions for 120 minutes, after which the gas was changed back to argon, and the furnace cooled.

The results of the reactivity tests are reported as fractional weight changes, calculated using equation 1.

$$\text{fractional weight change} = \frac{m_t - m_i}{m_i} \qquad (1)$$

Where m_t is the mass of the sample at time t and m_i is the initial sample mass. In the cases where minerals were present, the initial sample mass was the mass of the carbonaceous matter in the sample.

3 Results & Discussion

3.1 Coke Analogue with No Mineral Matter

The reactivity trials of the coke analogue were done under pseudo-CRI testing conditions. They were carried out at 1100°C under a carbon dioxide atmosphere for two hours. The repeatability of the reactivity test was assessed using the baseline material from two different batches. The weight loss curves are shown in Figure 2. The weight loss curves are almost linear over the period that the carbon dioxide was passed through the furnace and the extent of conversion is comparable to real coke during a CRI test. While there was some variability in the weight change curves, the final weight changes were found to vary by less than 3% from the average. There was some variability in the level of noise in the data, caused by the slightest contact between the crucible or suspension wire and the furnace itself. While this does not affect the average weight measurement, it can cause the measurement to be quite noisy. During the experiments, the sample was carefully positioned to remove this noise, but it some cases it was unfortunately unavoidable.
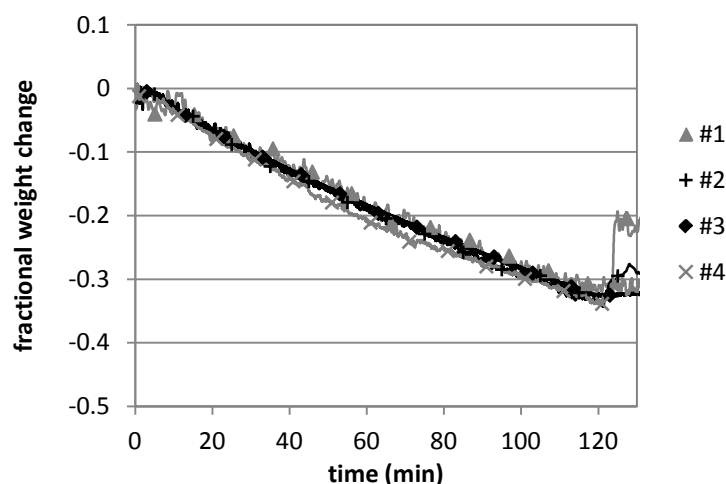

Figure 2. Fractional weight change curves for coke analogue samples with no mineral matter, fired at 1600°C, reacted with CO_2 at 1100°C for 120 minutes.

Typical microstructures of the baseline coke analogue containing no mineral matter, fired at 1600°C are shown in Figure 3. The microstructure of the coke analogue consists of a mixture

of somewhat rounded graphite particles and a more "stringy" binding carbon type. There was also another "smooth" carbon found in association with the "stringy" carbon. There are generally two different particle sizes found in the graphite, corresponding closely to the two different sizes of graphite used in the original mixture. The other carbon types found in the microstructure are formed by carburising of the phenolic resins during the firing of the coke analogue.
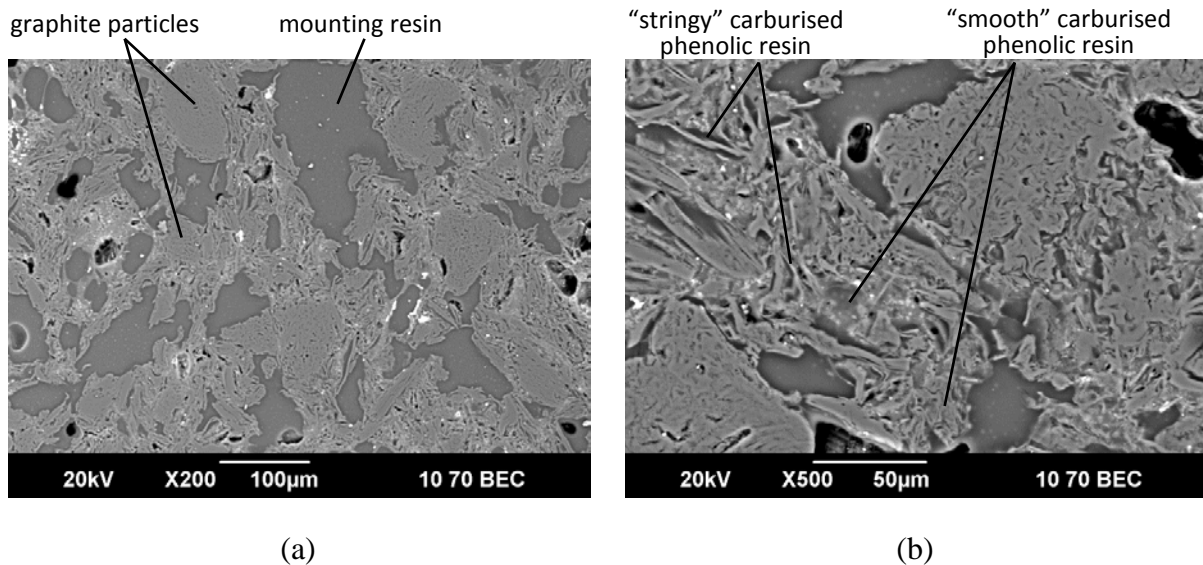

(a)   (b)

Figure 3. SEM images of coke analogue containing no mineral matter, fired at 1600°C. (a) low magnification; and (b) higher magnification image.

3.2 Mineral Additions to Coke Analogue

A major part of this work was to examine the possible effects of the addition of different minerals to the coke analogue on its reactivity. A summary of the reactivity data for the samples produced with different mineral additions is shown in Figure 4. The final fractional weight change is plotted against the amount of mineral addition. It clearly shows that the different mineral additions have had an effect on the reactivity of the coke analogue.
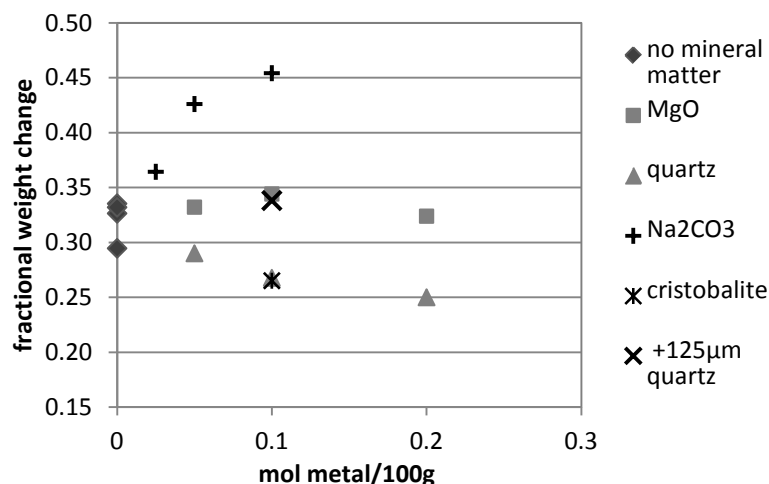

Figure 4. The final fractional weight change of the coke analogue samples after reaction with CO_2 at 1100°C for 120 minutes.

The bulk densities and apparent porosities of the different samples are given in Table 2. The bulk densities of the coke analogue samples were generally in the range of around 1000-1200 kg/m^3. The porosities of the majority of the samples were in the range of 39-50%. The

variability in the density and porosity measurements was approximately 5% of the measured value. The coke analogue that contained mineral matter was found to be more porous than that without mineral matter when fired under the same conditions. It was also noted that the porosity seemed to increase slightly as the addition of minerals increased. However, this change in the porosity with increasing mineral content was small.

Table 2. Densities and apparent porosities of coke analogue samples, measured by the buoyancy method.

Added Mineral/Variable	Amount (mol metal/100g) or variable value	Bulk Density (kg/m^3)	Apparent Porosity (%)
no mineral matter (no MM)	0	1096	39.8
MgO	0.2	1061	42.8
	0.1	1028	44.9
	0.05	1074	41.9
quartz	0.2	997	50.0
	0.1	1205	47.0
	0.05	1200	45.6
Na as Na$_2$CO$_3$	0.1	1262	66.4
	0.05	1253	65.0
	0.025	1271	64.6
cristobalite	0.1	1168	49.4
+125μm quartz	0.1	1041	44.4

3.2.1 Effect of Silica Additions to Coke Analogue

Quartz had the effect of reducing the reactivity of the coke analogue. Its effect on the reactivity of the coke analogue appeared to increase as the proportion of quartz in the sample increases. Silica was added to the coke analogue in several different forms. The effects of the addition of silica with different crystal structures on the reactivity of coke analogue were tested by additions of quartz and cristobalite. There was little difference in the reactivity between the coke analogue samples containing quartz and cristobalite. The similar effect of the silica additions to the coke analogue may be due to the conditions under which it is produced. The coke analogue is heated to 1600°C during firing. This may cause silica to change from one form to another. Consequently, it may have been possible that the final form of silica in both cases was the same. This possibility will form the basis of a future investigation.

The size of the mineral matter added to the coke analogue was also investigated, by the addition of quartz of two different size ranges. For the majority of the additions, the minerals were sized to -38 µm, including the quartz. For comparison, quartz in the range of -150 +125 µm was added to a coke analogue sample. These two size ranges represented two reasonably extreme cases for small and large mineral particles in coke. The size of the quartz addition was found to have had a significant role in the effect of the mineral addition to the coke analogue reactivity. While the smaller sized addition reduced the reactivity of the coke analogue, the larger sized addition had little effect on the reactivity. This is likely to be a surface or contact area effect. Smaller sized mineral matter would require many more particles for the same added mass than larger sized minerals, leading to an increased contact area between the mineral and the carbonaceous material, and increasing any reactivity effect.

The microstructure of a coke analogue sample containing 0.1 mol/100g quartz was investigated to determine the distribution of the mineral matter within the samples. The microstructure of a quartz sample is shown in Figure 5, along with the corresponding elemental map for silicon. The quartz is found to be distributed evenly throughout the sample. It was only found in the carburised phenolic resin. Areas with minimal silicon in the maps

correspond to both the mounting resin filled pores and graphite particles. The quartz was in the form of discrete particles, with a typical size somewhat smaller than 38 µm.

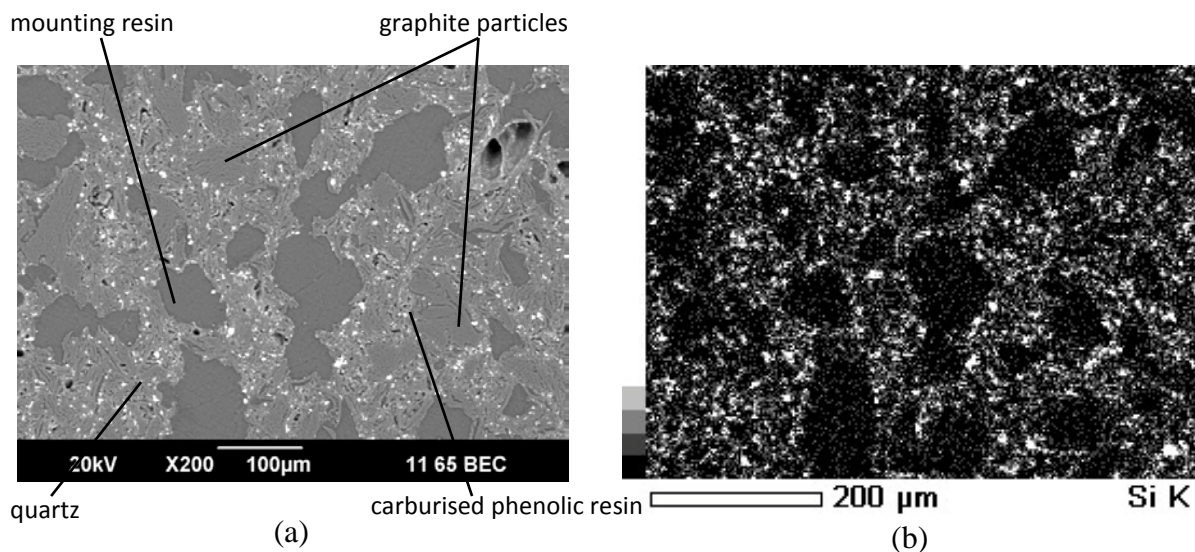(a)   (b)

Figure 5. SEM image and EDS elemental map for a coke analogue sample containing 0.1 mol/100g quartz. (a) Typical field of view at low magnification; (b) Si elemental map.

3.2.2 Effect of Magnesia Additions to Coke Analogue
Magnesia had the effect of slightly increasing the reactivity of the coke analogues. Increasing the amount of magnesia in the coke analogue did not seem to have a further effect on the reactivity of the samples.

3.2.3 Effect of Sodium Mineral Additions to Coke Analogue
The addition of sodium to the coke analogue increased the reactivity significantly. The increase in the reactivity of the coke analogue increased as the addition of sodium increased. It was expected that the coke analogues containing sodium carbonate would have higher porosities than other samples due to the decomposition of sodium carbonate during firing of the coke analogue (equation 2). The removal of the CO_2 would lead to higher porosity on its own, but may also have given rise to gasification of the surrounding carbonaceous material, by the Boudouard reaction (equation 3).

$$Na_2CO_3 \rightarrow Na_2O + CO_{2(g)} \tag{2}$$
$$CO_{2(g)} + C = 2CO_{(g)} \tag{3}$$

The porosity of these samples was much higher than any of the other samples, which precluded simple comparison with samples with other mineral additions. In addition to the increased porosity, there were also doubts about the amount of sodium minerals in these samples after firing. A significant amount of deposit was found at the upper end of the furnace. This deposit was analysed using an SEM-EDS system and found to be sodium rich. It is likely that this material was volatile sodium oxide which sublimes at 1275°C [10], significantly below the firing temperature of 1600°C. However, it was expected that some sodium would remain in the samples after firing. Despite this, it cannot be stated that any change in reactivity in the samples was merely due an increase in the porosity of the samples. The reactivity of the sodium samples did not exhibit simple linearity with the porosity of the samples. It may be possible that the sodium addition is having a further effect, either by some remaining sodium in the samples catalysing the gasification reaction, or by having an effect on the carbon structure during firing.

It was expected that the currently used coke analogue firing temperature of 1600°C would cause problems in developing representative analogues for testing minerals the undergo significant phase changes and vapour production at temperatures greater than nominal coke production temperatures of ~1000 to 1100°C. It would appear that Na based minerals fit this category.

3.2.4 Comparison of Coke Analogue to Coke
The effects of the addition of minerals to the coke analogue on reactivity follow those seen in coke. In a study based on the addition of minerals to a coal containing <1wt% ash, silica, magnesia and sodium carbonate were found to have similar effects on the reactivity as seen in the coke analogue [11].

3.3 Physical Effect vs. Chemical Effects

Due to the complex nature and variability of industrial coke it is often extremely difficult to separate the individual effects of key components important in cokes reactivity. While the addition of the minerals to the coke analogue had an effect on the reactivity of the samples, it also had an effect on the physical characteristics. The addition of minerals to the coke analogue increased the porosity of the samples. To assist in determining whether physical effects rather than chemical effects were determining the reactivity of the coke analogue, the final weight change of different samples was plotted against their porosities, shown in Figure 6.
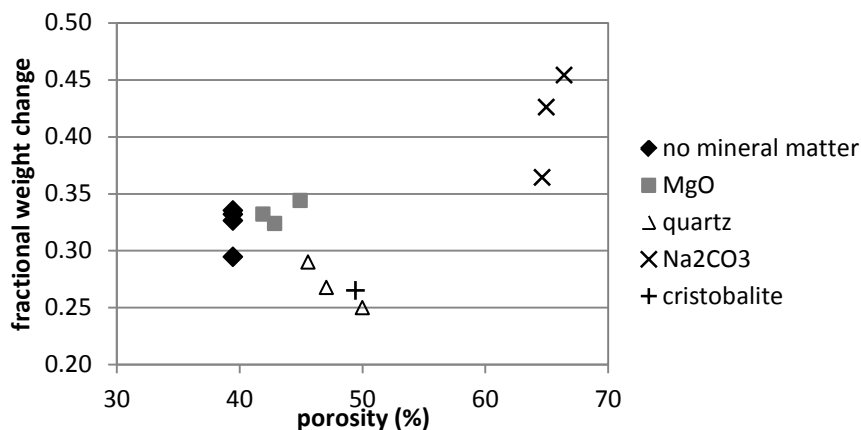

Figure 6. Final fractional weight change after reaction of coke analogue samples with different mineral additions, plotted against porosity.

There was a general trend for the reactivity of the samples to increase as the porosity increases. In general terms it can be stated that most coke reactions can be classified as heterogeneous kinetic reaction systems [3,6,7]. The rates of reaction in heterogeneous kinetic systems are proportional to the contact area between the reactants [12]. Therefore increases in contact area, in this case between the solids (minerals and carbon) and the gas phase, as a result of an increase in porosity would increase the rate of reaction [13]. It is also possible that the reaction could be partially diffusion controlled, so that increases in porosity reduce the resistance to gas pore diffusion, increasing the rate of reaction. However, for the samples with the quartz additions, the reactivity of the samples decreases as the porosity increases. This may be seen as evidence that the minerals present in the coke analogue are having an effect on the reactivity of the samples, in addition to any physical differences in the samples. Consequently, the results do indicate the use of the coke analogue enables simpler and arguably clearer delineation of the individual effects of key components in cokes reactivity.

3.4 Effect of Firing Temperature

To examine the effects of reducing the firing temperature from 1600°C, samples with no mineral matter were fired at 1100°C and 1300°C. The fractional weight changes after reaction at 1100°C with CO_2 and the porosity of the samples are shown in Figure 7. The reactivity of the sample generally decreased as the firing temperature increased. The apparent porosity of the coke analogues seem to be largely independent of temperature as the firing temperature increases between 1100 and 1600°C. The main change that can occur in the coke analogues as the firing temperature increases is the carburisation of the phenolic resins, which may be becoming more structured. This could be confirmed through further characterisation, by techniques such as Raman spectroscopy. Measurements of the crystallite size by XRD are thwarted by the presence of the graphite added to the original mixture, which obfuscates any changes that may be occurring.

In terms of a possible reduction in the coke analogue firing temperature, the results indicate that it should be possible to reduce the firing temperature of the coke analogue to at least 1300°C and possibly 1100°C in future studies.
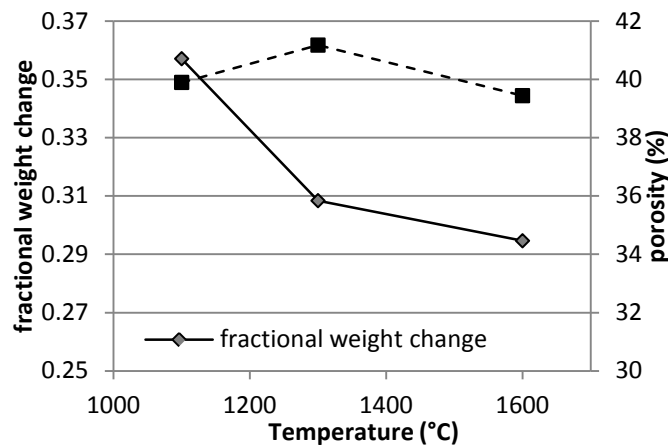

Figure 7. Fractional weight change after reaction and porosity of coke analogue samples fired at different temperatures.

4 Conclusions

A preliminary study has been conducted to test the suitability of coke analogue for studying the effects of minerals on the reactivity of coke. The coke analogue was found to replicate the behaviour of industrial or real coke, in that the mineral content had an effect on reactivity. While the addition of the minerals to the coke analogue also changed some of the physical properties, such as porosity, the presence of the mineral matter in the analogue played a role in determining the reactivity of the samples. The results presented give a strong indication that the coke analogue can be used as a research tool in better understanding the effects of the mineralogy of coke on its reactivity and strength.

- Quartz additions were found to decrease the reactivity of the coke analogue, while magnesia additions slightly increased it.
- The particle size of the mineral addition was found to also have an effect on the reactivity. While small sized (-38 µm) quartz reduced the reactivity of the coke analogue, larger sized particles (-150 +125µm) had little effect on the reactivity.
- The addition of quartz and cristobalite to the coke analogue both had similar effects on the reactivity. Consequently, the results did not provide any clarification on the role of different initial crystal structures of silica on the reactivity of the coke analogue.

- The addition of sodium increased the reactivity of the coke analogue dramatically. The increase in the reactivity does not seem fully explained by the increase in porosity caused by the addition. Further characterisation of these samples may be necessary to fully understand the effect of the sodium addition.

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