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Abstract

The gasification rate in CO₂ of the coke analogue containing calcium oxide was studied using analogues doped with alumina (corundum), calcium aluminates (CA6, CA, C3A) and lime minerals. The coke analogue is a laboratory material with simplified carbon structure that has a mineral component with a particle size, size distribution and mineral dispersion that can be controlled. The main focus of this study was to quantitatively assess the effect of calcium in the mineral on the analogue's reactivity. The analogues were reacted with CO₂ isothermally in the temperature range of 1173–1623 K. It was found that the reaction rate increased with increasing CaO activity/number of moles of Ca in the mineral. The relative reaction rates (from lowest to highest) of the analogues doped were alumina, CA6, CA, C3A and lime. The relative apparent activation energies of the gasification from lowest to highest was lime, C3A, CA, CA6 and alumina.

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1 **The Effect of Calcium Aluminates on the Coke Analogue Gasification**

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8

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21 Key words: Coke analogue, Calcium aluminates, TGA, Coke kinetics, Rate of reaction

22 Nomenclature

23 X Carbon conversion

24 R_C Initial apparent reaction rate, $\text{g g}^{-1} \text{s}^{-1}$

25 T Temperature, K

26 dt Reaction time, s

27 W_0 Initial mass of the sample, g

28 W Mass at time t, g

29 dW Mass change during the reaction, g

30

1. Introduction

Metallurgical coke is a key reagent used in blast furnace iron production. It is the fuel for the furnace, the source of reductant for the iron ore and aids control of permeability in the furnace [1]. Coke is a complex material, composed of different forms of carbonaceous materials, minerals and has an intricate pore structure. It also is inherently heterogeneous with respect to most metrics used to characterise it.

The mineral component of metallurgical coke is of the order 10 to 12 mass % and comprises of elements such as O, Si, Al, Fe, Ca, S, Mg, K, Ti and Na [2-4]. Though less common, the minerals may also contain P, Mn, C, H, N, Ba, Sr, F and Cl [5]. Minerals containing oxides of alkalis [3, 6-9] and transition metals [2, 3, 7, 10, 11] can increase coke gasification/ reactivity. Calcium-bearing minerals are of particular interest in coke/coal studies. It has been shown to be particularly mobile in coal and coke [12-15] and significantly affects coke reactivity. Well-known calcium-containing minerals in coke are oldhamite (CaS), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), akermanite ($\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$) and diopside ($\text{MgCaSi}_2\text{O}_6$) [16].

When exposed to high temperatures and reactive atmospheres, the inherent complexity and heterogeneous nature of coke make it difficult to isolate the effects of specific components on coke behavior and reaction kinetics [17-19]. To overcome the complexity and heterogeneity issues associated with studying the reactivity of metallurgical coke, a coke analogue has been developed. The mineral component in the analogue can be controlled with respect to phase, composition, particle size and dispersion throughout the analogue. This analogue has previously been used in studies to distinguish the relative reactivities of coke analogues doped with different minerals [18, 20], the dissolution rate of coke in liquid iron [19, 21, 22], kinetic mechanistic studies of reaction in CO_2 , isolating specific CaO/lime [15] effects on the coke analogue reactivity and demonstrating it had similar gasification reaction behaviour to that of metallurgical coke [23, 24].

The focus of this investigation was to assess the effects of calcium added as a simple oxide or as a calcium aluminate on the gasification kinetics of the coke analogue in CO_2 . Three calcium aluminates,

CaO.6Al₂O₃ (CA6), CaO.Al₂O₃ (CA) and 3CaO.Al₂O₃ (C3A), lime (CaO) and alumina (Al₂O₃) were used to represent the mineral (ash) component of the analogue. The choice of minerals was a compromise, dealing with minerals of some relevance to metallurgical coke but less complex than those found in metallurgical coke. This simplified mineral component of the analogue allowed the focus of the effects of Ca and Al oxides/minerals on coke reactivity in the absence of interference from other components such as Mg, F and PO₄³⁻ that have been identified to also have effects on coke gasification.

2. Experimental

Coke analogue samples were reacted with CO₂ in a thermogravimetric analysis (TGA) set-up (Fig.1) to assess the effects of selected minerals on the coke gasification kinetics.

Five different coke analogue batches were prepared using either a calcium aluminate (CA6, CA or C3A), Al₂O₃ or CaO. The minerals were added to give a constant concentration of 0.1 mol cations/100 g in the analogue and were sieved prior to the addition to give a constant particle size range of 38 – 53 µm. Experiments were carried out for 2 hours isothermally in the temperature range of 1173 – 1623 K.

The calcium aluminates were chosen based on the Al₂O₃-CaO binary system (Fig. 2). The choice of minerals allowed the evaluation of the specific effects of CaO as a separate phase and of CaO bonded/complexed within a mineral.

2.1. Reaction rate measurements

An unreacted coke analogue sample was weighed and placed in the furnace hot zone on an alumina pedestal suspended from a balance. This was then heated at 10 K/min to the desired temperature under Ar flowing at 1 L/min. Once the reaction temperature was reached, the gas was changed from Ar to CO₂ and set at a flow rate of 4.5 L/ min. The changing over of the gas was defined as the start of the experiment. The flow rate was chosen/ established to ensure the reaction kinetics were independent of gas flow (i.e. eliminate gas film diffusion control) [23]. The gases used were 99.99% pure and passed

through ascarite and drierite prior to entering the TGA. When running with Ar, the gas was also passed through Cu turnings at 573 K to minimise oxygen entering the furnace.

The recorded weight change during the reaction as measured by the TGA was used to calculate the carbon conversion, X (eq. 1), and initial apparent reaction rate, R_C (eq.2).

$$X = \frac{W_0 - W}{W_0} \quad (1)$$

$$R_C = \frac{1}{(1-X)} \frac{dX}{dt} \quad (2)$$

2.2. Preparation of coke analogue

The coke analogue was prepared using carbonaceous materials (laboratory grade graphite, phenol-formaldehyde resins (Bakelite and Novolac resin in propylene glycol) and hexamethylenetetramine (HTMA)) and minerals (CA6, CA, C3A, alumina or lime). The ingredients were mixed and pressed to form a cylinders of ~30 mm height and 18 mm diameter samples. These cylindrical samples were then cured for 24 hours in an oven at 443 K and then fired in a two-stage process. In stage 1, the analogue was fired at 1273 K for 1 hour. In stage 2, the analogue was fired at 1473 K for 1 hour.

A fired coke analogue sample from each batch was cross-sectioned, mounted in epoxy resin, polished and carbon coated for SEM analysis. The CA6, CA, C3A and lime doped coke analogue samples were treated as water sensitive and prepared using, water-free alcohol based polishing lubricants. These samples were used in optical porosity and SEM/EDS characterisation.

The initial porosity of all the coke analogue samples was measured using an optical porosity method (detailed elsewhere [20]). The initial porosities of the samples (10 – 500 μm pore diameter range) prior to the gasification in the TGA were in a narrow range of 30 – 33 %. This technique had a pore diameter lower limit of ~10 μm . It is desirable to maintain the initial porosities in a narrow range to minimise the effect of porosity on the measured analogue reactivity. This should

aid elucidation of the specific effects of mineralogy on reactivity.

2.3. Preparation of the mineral phase

High purity (+ 99.9 %) laboratory grade Al_2O_3 and CaCO_3 powders obtained from Sigma Aldrich were used in the production of the mineral phases.

The calcium aluminates were prepared by mixing Al_2O_3 and CaCO_3 powders in appropriate proportions and fired to produce pellets of calcium aluminates. CaCO_3 was used instead of CaO to overcome issues associated with CaO moisture absorption, allowing accurate weighing of the carbonate. The powders were first mixed with 500 ml of deionised water to make a slurry. They were then filtered using a 75 mm Büchner funnel and a Filtech 2850 – 70 filter paper equivalent to Whatman #6 (pore size 3 μm). The resulting filter cake was then oven dried at 373 K for 24 hours. Deionised water (2 mass %) was added as a binder to the dried filter cake prior to pressing into pellets. Approximately 8 g of the mixture was pressed in a 25 mm diameter steel die under a 1.3×10^8 Pa pressure. The pellets were then fired in a muffle furnace at the temperatures listed in Table 1. The firing temperatures for the calcium aluminates were chosen based on the phase diagram given in Fig.2. The pellets were then crushed and sieved to get the particle size of 38 – 53 μm .

CaO was prepared by heating CaCO_3 in the air to 1273 K in a muffle furnace. To minimize the moisture pick-up the calcined CaO was cooled and stored in a vacuum desiccator. The CaO was sieved to get particle size of 38 – 53 μm and added to the coke analogue as quickly as possible to reduce the potential moisture pick-up.

Alumina particles in the size range of 38 – 53 μm were prepared by sintering the <10 μm as received alumina powders from Sigma Aldrich. The as-received alumina powder was mixed with 2 % deionized water prior to pressing into pellets. The pellets were made by pressing approximately 8 g of alumina powder + deionized water mixture in a 25 mm diameter steel die under 1.3×10^8 Pa pressure. These pellets were heated to 1973 K for 12 hrs. The pellets were then crushed and sieved to get the particles sizes required.

Post-mineral preparation of all minerals phases was confirmed by XRD prior to the addition to, and in the fired state of, the coke analogue. No significant change in the mineral was observed, see Fig. 3 for the XRD patterns of the added minerals.

3. Results and Discussion

3.1. Reactivity studies using minerals doped coke analogues

The initial apparent reaction rates, R_C , were calculated for the analogues and plotted against $1/T$ and the results are given in Fig. 4. From this figure, it can be seen that over the temperature range tested (1173 – 1623 K), R_C increased with increasing temperature. Further, similar to that previously reported for the base analogue with no mineral addition, [23, 25] lime doped coke analogue [15] and that of metallurgical coke [26, 27], two reaction zones were identified. These zones were established using the method developed by Walker et al [26]. In this method, the linearity of the curves in the plot given in Fig. 4 are used to define the reaction zones. The transition from zone I (chemical reaction control) to zone II (Chemical reaction + pore diffusion control) was in the range of 1330 – 1400 K. There was no strong correlation between the transition temperature and the calcium content in the coke analogue.

Fig. 5 shows the comparison of $\ln R_C$ and $1/T$ of the coke analogue samples studied. From this figure it can be seen that R_C increases with increasing Ca content of the mineral, i.e. R_C for alumina < CA6 < CA < C3A < lime.

To assess the effect of Ca on the reactivity plots of the total number of moles of Ca (n_{Ca}) versus R_C (Fig. 6) and the chemical activity of CaO (a_{CaO}) versus R_C (Fig. 7) were made. MTDATA [28] was used to evaluate a_{CaO} . The reference state used for CaO was halite (monoxide). The n_{Ca} and the a_{CaO} for the respective minerals at the different temperatures are given in Table 2. Temperatures representative of zone I (1223 K) and zone II (1623K) have been considered in this comparison. The solid line in the Fig.s represent the best fit linear regression of the data.

From the Figure, it can be seen that there is a stronger correlation with R_C and n_{Ca} than that for a_{CaO} as

indicated by the higher R^2 . This would tend to indicate that the Ca effect is simply a mass effect rather than a chemistry effect associated with the bonding in the mineral phase. Both approaches show that their effect is greater at higher temperatures as indicated by the increased slope of the regression lines at higher temperatures.

Notwithstanding the distinction between n_{Ca} and a_{CaO} on R_C , the data shown in Figs 6 and 7 are in general consistent with that reported in the literature [29-32] on the effects of Ca in the ash on the rate of coke gasification. It is not clear why the R_C is a linear function with the Ca content. This will be discussed in more detail in the mechanistic section 3.3.

The effect of temperature was further analysed by calculation of activation energies for zones I and II (see Table 3). The activation energies for both zones decrease with the increasing Ca content of the mineral in the analogue. This is indicative of the strong catalytic effect of Ca on the gasification and is consistent with what others have reported for Ca effects on gasification for metallurgical coke [18, 29, 31-34].

3.2. Mineral dispersion in the coke analogues – SEM studies

Fig. 8 shows SEM backscattered images and EDS maps for the coke analogues in their fired condition prior to the gasification reaction. In the micrographs in Fig. 8a (alumina) and Fig. 8b – d (calcium aluminates) the shape and size of the particles in the coke analogue were of similar nature (size and morphology) to those added to the green analogue i.e. the particles have not changed significantly on firing. With the lime addition (Fig 8e), the particles were reduced in size and more dispersed throughout the analogue. In a previous study focused on the effects of lime addition to the analogue it was found that the lime had reacted with the analogue during preparation [15]. The reaction of lime on firing was explained in terms of an acid-base reaction [15] similar to that found in low ranked lignite coals [35-37]. More specifically, the strongly basic lime is reacting with the weakly acidic phenolic (Novolac) resin. This resulted in a greater dispersion of the lime throughout the analogue compared to the other minerals added to the analogue, a significant reduction in the lime particle size and a significantly increased contact area between the lime and the carbon in the

analogue. There was no apparent increase in the analogue porosity from the lime addition.

Why does the lime show significantly different behaviour in the analogue to the other calcium-bearing minerals (CA6, CA, and C3A)? While the answer is not clear it is likely related to the relatively higher acidity of alumina compared to the acidic entities (phenolic groups) present in the phenolic resins. This may result in a stronger bond with the alumina than the phenolic resin.

In addition to the amount/concentration of minerals, the reactivity is also a function of particle size and the distribution of the mineral phase [2]. In this study, attempts were made to fix particle size and distribution to elucidate the effects of mineral type on the reactivity of the analogue. The fact that the lime particle behaviour was significantly different during the preparation from the other minerals, reducing in size, makes this problematic. It is likely the lime effects on reactivity at the nanoscale are more complex than simple particle size-contact area analysis allows. In spite of this, the results excluding lime, and focusing on only the alumina and calcium aluminates, still indicate that increasing the Ca level in the analogue increases reactivity.

3.3. Discussion of rate controlling mechanism

Generally, the carbon – carbon dioxide gasification reaction mechanism can be expressed as Eq. 3 and 4 [39-45].

where; C_f = active carbon site

$C(O)$ = surface oxygen complex

j_1, j_2 and j_3 = rate constants

In the first step (Eq.3), CO_2 dissociates into CO forming a surface oxygen complex C(O). In the

second step (Eq.4), the surface oxygen complex produces another CO molecule leaving a free C active site for further reaction. The second step is considered as the rate controlling step [41, 46].

There are two widely accepted mechanisms to explain the increasing reactivity of gasification reactions, an oxygen transfer mechanism and an electron transfer mechanism [8, 47, 48]. The electron transfer mechanism is suggested for the transition metals bearing systems. It is based on the ability of transition metals to accept an electron to influence the distribution of π electrons in the carbon surface [49]. The oxygen transfer mechanism is suggested for the reactions that are affected by metals and metal oxides where the catalytic surface chemisorbs an oxygen atom from CO_2 to transfer to the carbon site later on [8, 50].

Ca, as a non-transition metal, most probably followed an oxygen transfer mechanism. Some researchers have suggested different reactions for Ca catalysis in carbon gasification. Those involve formation of CaCO_3 (reaction 5 and 6) or CaO.O (reaction 7-9) or CaC_2 (reaction 10) [51-54]. The formation of these species at the high temperatures used in this study was thermodynamically assessed by consideration of the ΔG° of reactions 5, 7 and 10 over a range of temperatures (see Fig. 9). The ΔG° 's were calculated using the reaction module of FactSage 7.0 [55]. In the FactSage calculations, CaO.O is represented by CaO_2 . Reactions 5 to 9 were thermodynamically assessed in a previous publication [15]. To aid clarity and understanding this assessment has been included here for comparison with reaction 10.

It was found that the reactions all had a $\Delta G^\circ > 0$ for the temperature ranges evaluated in this study. It is therefore unlikely that these reactions occurred during the gasification experiments.

It is known that the presence of Ca in coke ash can increase the amount of active sites ($C_{(f)}$) [45]. The enhanced reaction rate is attributed to the increased number of active sites ($C_{(f)}$) that favour carbon dioxide dissociation. From a molecular modeling study, it was found that calcium interacts exothermically with the carbonaceous lattice [56]. These interactions are thought to cause the increase in the electron density of carbon, increasing the number of active carbon sites (Eq.3). This increase in active sites ($C_{(f)}$) offers a plausible explanation of why Ca increases the reactivity of the coke analogues in this study.

This catalytic mechanism may explain the increasing reactivity with increasing Ca content. It may also explain why the R_C is a linear function with the Ca content (Fig. 6). The contact area between the minerals and the carbon in the analogue is, with the exception of lime, reasonably controlled due to the control of particle size addition of the minerals. Therefore, the Ca in the mineral associated with this surface is likely proportional to the mineral Ca content. This could explain the linear effect, though more work is required to confirm this possibility.

The catalytic mechanism does not explain the observed decreased apparent activation energy. At this point, there is no clear understanding of the reason for the decreasing activation energy.

Further studies will focus on testing the possibilities of the changing reaction mechanism from both a theoretical and experimental perspective. The effect of other minerals commonly available with Ca in metallurgical cokes, such as SiO_2 and MgO , will also be considered.

4. Conclusion

The effect of calcium aluminates (CA6, CA and C3A) on the coke analogue gasification kinetics was studied. The results were compared with lime doped and alumina doped coke analogues gasification. Calcium aluminates were observed to increase the reaction rates with increasing CaO activity/number

of moles of Ca. The relative reaction rates (from lowest to highest) of the analogues doped with minerals were alumina, CA6, CA, C3A and lime. The relative apparent activation energies of the gasification vary, from lowest to highest, lime, C3A, CA, CA6 and alumina.

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Table 1:

Calcium aluminate type	Firing temperature / K
CA6	1898
CA	1823
C3A	1623

Table 2:

Mineral	Number of moles of Ca in 100 g of base coke analogue	Activity of CaO at 1223 K	Activity of CaO at 1623 K
Alumina	0.000	0.0000	0.0000
CA6	0.007	0.0015	0.0012
CA	0.031	0.0400	0.0800
C3A	0.055	0.6720	0.6000
Lime	0.100	1.0000	1.0000

Table 3

Coke analogue	Apparent activation energy / kJ mol ⁻¹	
	Zone I	Zone II
Alumina doped coke analogue	231.3 ± 1.8	63.1 ± 0.3
CA6 doped coke analogue	204.4 ± 1.5	39.5 ± 0.4
CA doped coke analogue	159.9 ± 1.7	37.8 ± 0.3
C3A doped coke analogue	146.3 ± 1.8	34.5 ± 0.3
Lime doped coke analogue	119.8 ± 1.5	20.7 ± 0.3

Fig.1.

Fig.2.

- 1 – CA2 + Oxide liquid
- 2 – CA + Oxide liquid
- 3 – C3A + Oxide liquid
- 4 – CA6 + Corundum

Fig.3.

Fig.4.

Fig.5.

Fig.6.

Fig.7.

Fig.8.

Fig.9.