



COOPERATIVE RESEARCH CENTRE FOR COAL IN SUSTAINABLE DEVELOPMENT
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**THE EFFECT OF SELECTED COAL PROPERTIES ON COKE
GASIFICATION**

TECHNICAL NOTE 29

Author:

Mihaela Grigore

The University of New South Wales

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QCAT Technology Transfer Centre, Technology Court
Pullenvale Qld 4069 AUSTRALIA
Telephone (07) 3871 4400 Facsimile (07) 3871 4444
Email: Administration@ccsd.biz

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| | |
|---|------------------------|
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| The University of Newcastle | Prof Barney Glover |
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1. Introduction

The blast furnace is continuing to evolve under the twin pressures of cost and greenhouse gas requirements. The amount of coke required to produce one tonne of hot metal has been reduced to levels unheard of fifty years ago. Yet even now, there is room for improvement. Low temperature furnaces and high-oxygen furnaces are being investigated as the way of the future. These furnaces will set new demands on the coke that is used. One of the demands is designing cokes with a reactivity that is suitable for these new furnaces. But in order to be able to do that effectively, the relationships between the reactivity of the coke and other properties of the coke must be understood better.

There are continuing efforts to identify and control the factors that determine the reactivity of coke. Factors such as rank of the starting coal, maceral composition of the starting coal and the composition of the ash, which are known to affect coke reactivity and strength, are routinely determined. Yet these factors alone are not enough to determine coke reactivity (Coin, 1995). A number of cokes perform better (and some substantially worse) than expected from the values of these factors. Other factors, as yet unquantified, are also important. This study was initiated to identify these other factors. This project was assisted by the recently developed ability to quantify the mineral matter present in coke – mineral matter is expected to affect coke quality but until now has not been quantified.

In this report we present some of the major findings of this study, and discuss some implications of these findings. Full details of the experimentation and results may be found in M. Grigore's PhD thesis.

2. Objectives

- To assess the importance of coke properties on coke gasification
- To assess the influence of coal rank, maceral composition and mineral matter on coke properties

3. Procedure

Nine Australian bituminous coals that are used in coking coal blends were selected to have a range of rank, maceral composition and ash and mineral matter composition. They were carbonised in the CSIRO 9kg cylindrical retort. The cokes were crushed and the 0.6-1.0 mm fraction was reacted with 100% carbon dioxide at approximately 900°C. The raw and reacted products were characterised by surface area, carbon crystallite size and mineral matter composition. Maceral concentrates were prepared from 4 coals and they were coked in a 70 g furnace. The raw carbonised macerals

were also characterised by surface area, carbon crystallite size and mineral matter and their reactivity to carbon dioxide was also measured.

As a world first, quantification of the mineral matter in cokes and their reacted products was established with an accuracy of better than 0.3%.

4. Main findings

For these coals and maceral concentrates

The reactivity of the cokes to carbon dioxide is not related to coal rank for these bituminous coals.

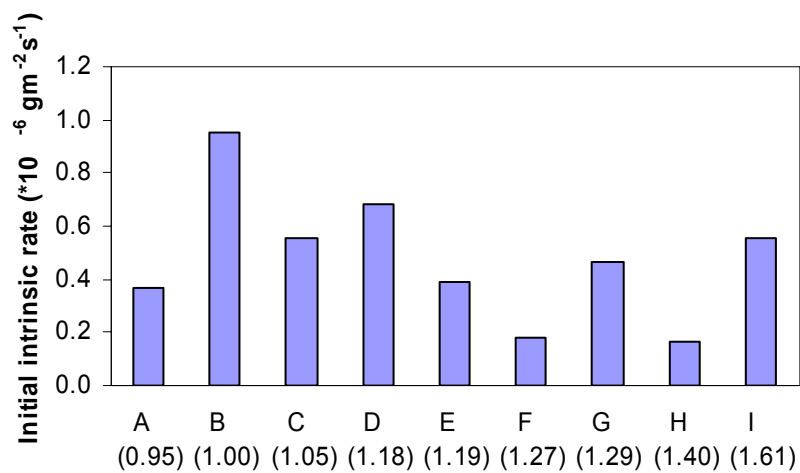


Figure 1. Initial intrinsic rate of cokes investigated. Cokes are tabled in order of increasing rank, given by mean maximum vitrinite reflectance (in brackets).

Reaction rate was unaffected by carbon crystallite size of the carbonised maceral-rich fractions (Figure 2). The greater reactivity of the carbonised inertinite-rich fractions appeared to be mainly due to their greater mineral matter concentrations and to some extent due to surface area, not anything intrinsic to the organic part of the inertinite.

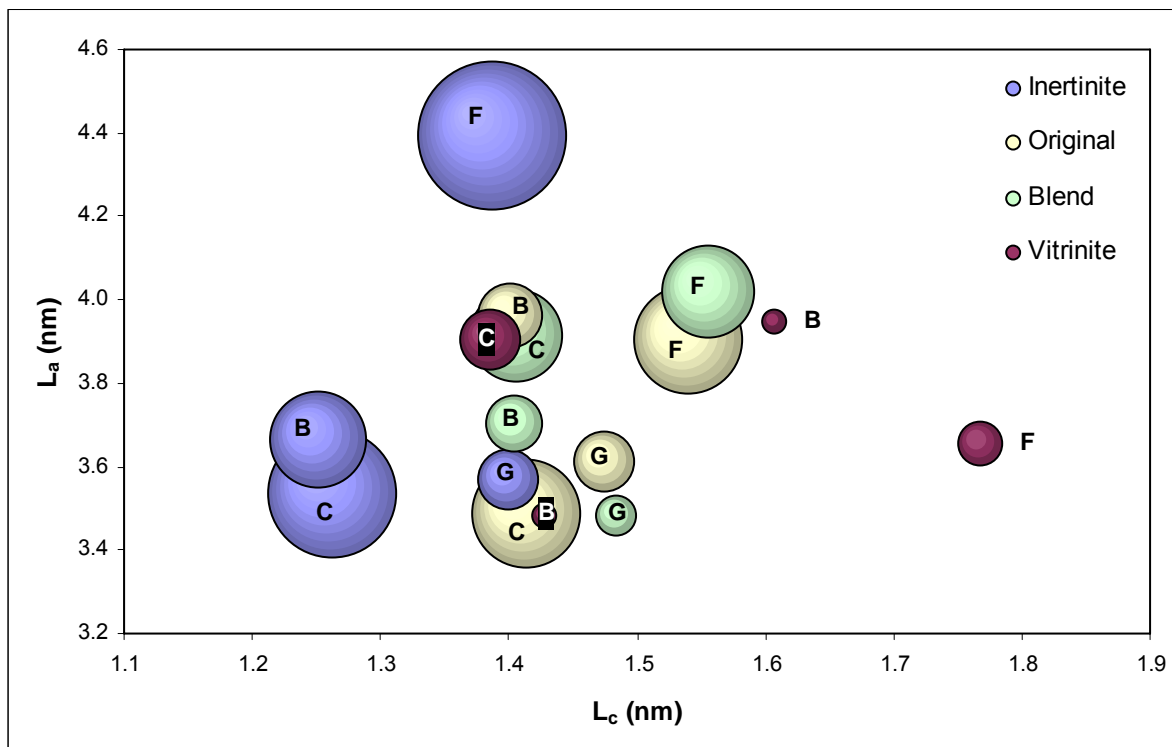
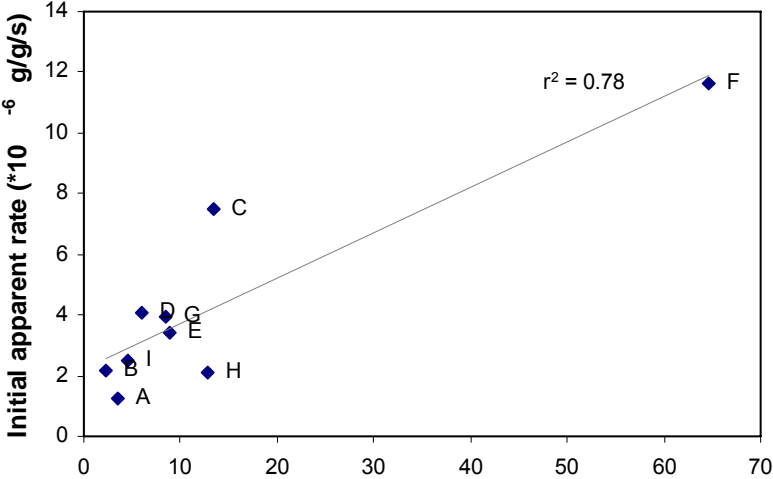
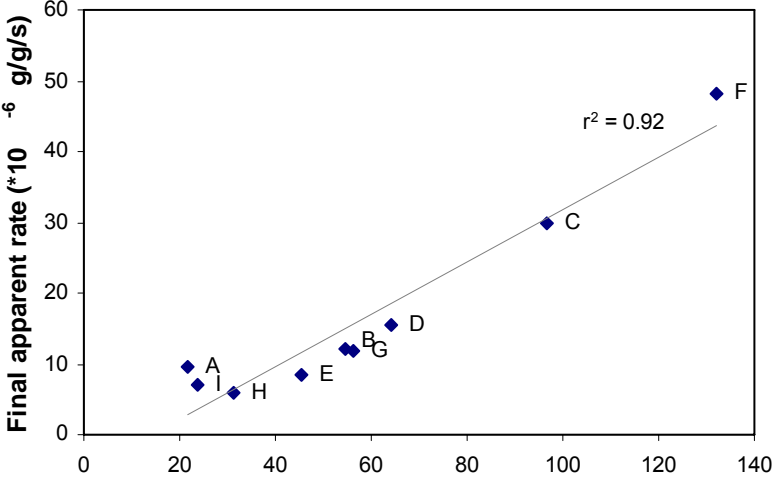


Figure 2. Bubble plot of initial apparent rate of reaction versus crystallite height (L_c) and width (L_a) in the coke. Larger bubbles indicate greater apparent reactivity.

Micropore (0.4-1.6 nm) surface area of coke, as measured by carbon dioxide, appeared to have little effect on the reactivity in the early stages of reaction with carbon dioxide, but its importance increased with increasing burnout, and as surface area increased (Figure 3). Surface area of the larger micropores and mesopores (0.8-150 nm) measured by nitrogen did not account for the observed difference in the reaction rate between coke.



a)



b)

Figure 3. Apparent rate of reaction at start (a) and after 15% burnoff (b), plotted against surface area.

Because the mineral matter in cokes was quantified with high accuracy, a number of new findings were made relating to the mineral matter:

The apparent reaction rate increased with increasing amounts of catalytic minerals such as metallic iron, pyrrhotite and iron oxides.

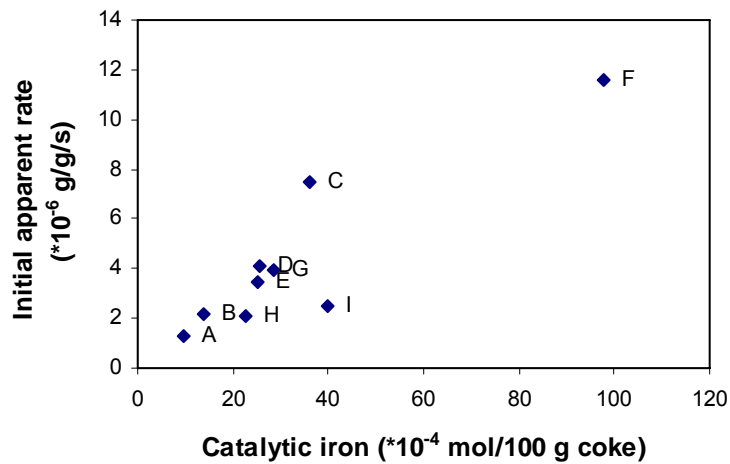


Figure 4. Relationship between initial apparent rate of reactivity of coke at 900 °C and amount of iron present as catalytic material. The major deviations from the line of best fit are cokes C and I. Coke I was found to have its iron in a form that was ~10 times bigger in the coke than coke C.

The catalytic iron phases (iron, iron oxide and iron sulfide) become inactivated during gasification; they interacted with other minerals producing as a result new mineral phases which did not catalyse gasification.

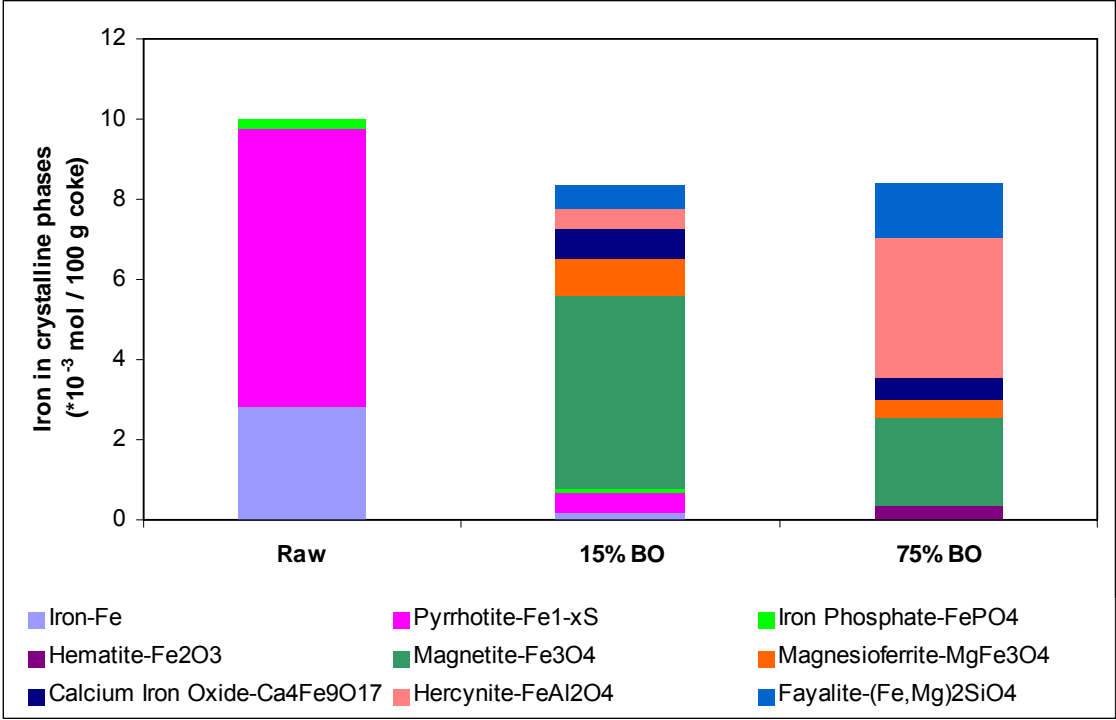


Figure 5. Mineral matter forms of iron in crystalline phases in coke F as a function of burnoff.

Exposure to carbon dioxide at 900 °C significantly changed the amounts of all mineral matter in the coke, except quartz (Table 1).

Carbon dioxide modified the mineral matter in coke much more than an equivalent temperature exposure in inert atmosphere (N₂) did.

A major contribution to the change is the oxidation of iron forms in the mineral matter, but other transformations, not directly related to iron oxidation states, were identified as well.

Table 1. Minerals in coke before treatment, after being exposed to nitrogen at 900 °C for 15 hours (annealed), and after being exposed to carbon dioxide at 900 °C for 15 hours.

| Mineral phase | Chemical formula | Raw (%) | Raw annealed (%) | 75% Burn-off (%) |
|--------------------|---|-------------|------------------|------------------|
| Anatase | TiO ₂ | 0.2 | 0.1 | |
| Diopside | CaMgSi ₂ O ₆ | 0.3 | 0.4 | |
| Iron Phosphate | FePO ₄ | 0.3 | 0.2 | |
| Pyrrhotite | Fe _{1-x} S | 5.0 | 3.0 | |
| Iron | Fe | 1.7 | 0.8 | |
| Oldhamite | CaS | 1.5 | 0.7 | 0.2 |
| Fluorapatite | Ca ₅ (PO ₄) ₃ F | 3.7 | 2.5 | 0.8 |
| Rutile | TiO ₂ | 0.3 | 0.6 | 0.3 |
| Quartz | SiO ₂ | 34.2 | 29.7 | 28.4 |
| Mullite | Al ₆ Si ₂ O ₁₃ | 6.0 | 3.0 | 9.8 |
| Akermanite | Ca ₂ MgSi ₂ O ₇ | 0.3 | 0.5 | 0.9 |
| Spinel | MgAl ₂ O ₄ | 0.6 | 1.8 | 4.3 |
| Anorthite | (Ca,Na)(Si,Al) ₄ O ₈ | | 0.5 | 2.4 |
| Fayalite | (Fe,Mg) ₂ SiO ₄ | | 0.9 | 1.4 |
| Hercynite | FeAl ₂ O ₄ | | 0.4 | 6.2 |
| Magnetite | Fe ₃ O ₄ | | 0.3 | 1.7 |
| Magnesioferrite | MgFe ₃ O ₄ | | 0.3 | 0.4 |
| Calcite | CaCO ₃ | | | 0.2 |
| Calcium Iron Oxide | Ca ₄ Fe ₉ O ₁₇ | | | 0.6 |
| Cristobalite | SiO ₂ | | | 0.9 |
| Hematite | Fe ₂ O ₃ | | | 0.3 |
| Leucite | KAlSi ₂ O ₆ | | | 0.3 |
| Rankinite | Ca ₃ Si ₂ O ₇ | | | 1.4 |
| Amorphous | | 46.0 | 54.1 | 39.4 |

Context

Implication of results on predicting coke reactivity

It is well known that coal rank and fluidity are important in predicting the reactivity and strength of the coke. But even if they are optimised the reactivity of the coke still can vary significantly. There have been many attempts to generate a robust equation for predicting CRI. It was suspected in the past that the reason for their failure to be general is that other variables that the equations did not include could also be important.

We have now shown that the type of mineral matter is important in predicting the reactivity of the coke (this has been suspected in the past, but this is the first demonstration of a tight connection between the mineral matter in coke and its reactivity).

In other words, if you want to predict the reactivity of a coke, you have to know the amount and forms of the iron that is present in the coke.

But this is not enough. The association and size of the iron particles is also important: finely dispersed iron results in more reactive coke than coarsely dispersed iron.

The results do not exclude the possibility of other catalysts (calcium-bearing minerals such as lime derived from the decomposition of calcite) contributing to reactivity, but the amount of active calcium minerals in these cokes was small.

We have demonstrated the relationship between iron and reactivity. However, what we also found is that two things happen during reaction with carbon dioxide: the catalytic material becomes physically separated from the coke, and the catalytic forms of iron are inactivated, probably by reaction with silicates. But the damage is done in the early stages of reaction. High iron cokes produce high surface area products on reaction and this means the carbon dioxide can penetrate faster and thus react faster. So it is important to know the composition of the mineral matter in the coke at the start.

This study has also shed light on the continual question of “how come inertinite-derived material in coke burn out much faster than the vitrinite-derived material?” The results show clearly that the increased burnout of inertinite-derived material in the NSC furnace is largely due to its greater mineral matter content and not strongly related to its poorer carbon ordering.

Implications for coal selection and control

Quite obviously, since the presence of iron, iron sulfides and oxides are important, it is best to minimise their amounts in the coke. This can be done by altering coal preparation conditions or, alternatively, coal sources. It is also feasible that since some iron silicates appear to be relatively inactive, an increased association between iron and silica bearing materials may prove to be an advantage in coke (but this possibility remains to be tested).

Certainly, it now appears important that the levels of these materials ought to be monitored, as an extra variable that could affect coke behaviour.

Such an influence of iron on coke reactivity destroys any chance of artificially adding iron minerals to coal blends as a method of introducing more iron into the blast furnace ('ferrocake'); the resulting increased reactivity of the coke is a major disadvantage. The reaction of iron minerals with coke oven walls, forming iron silicates at relatively low temperatures, also renders 'ferrocake' impractical.

One other major finding is that the mineral matter composition in the coke is affected by both heating and cooling conditions. Monitoring the amount of oxidised iron in the coke could assist in monitoring quenching processes so that there is a minimum of coke oxidation. Additionally, this opens the possibility of control of mineral matter in coke by the preparation conditions and its treatment afterwards. It is likely that in a non-recovery coke oven the mineral matter assemblage may be different again.

Implications for sustainability

One overarching aim of this project is to improve the sustainability of the blast furnace. This study has shown that additional criteria are necessary to characterise the coke for it to be best matched to blast furnace conditions. If iron levels and iron mineralogy are better controlled, or at least monitored, then the blast furnace should become more efficient, with better quality coke being used. In the future planned modifications to blast furnace operation, this is becoming increasingly important.

Hopefully, the increased knowledge should help address the problems that blast furnace operators have in identifying the source of problems in raw materials, when they arise.

Further work

This investigation is by no means a finished product. Further study is being investigated to identify if the different forms of iron have different catalytic effects. Mineral matter association is also important; it may prove to be as important as the total amount of catalytic iron in the coke, if this study is extended to include more than just Australian coals (i.e. further characterisation of the world coles!)

The reactivity study was done under conditions that allow penetration of carbon dioxide throughout the coke. In real conditions, even in the NSC test, this does not occur. It is probable that mineral matter may face oxidising conditions at the coke surface and reducing conditions in the coke interior: both will have different effects on the mineral matter and its behaviour in the coke. To explain coke behaviour in a blast furnace will require further study.

However, this study has demonstrated that

- mineral matter varies considerably between coles (more than ash composition),
- coke properties are deeply dependent on the nature of the mineral matter it contains, and
- if we want to predict coke reactivity, mineral matter in coke must be quantified.

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