1. Introduction

Liquid iron in the ironmaking blast furnace picks up more than half of its carbon while percolating through the packed coke bed in the deadman and heath of the blast furnace. Consequently, the rate of carbon dissolution into liquid iron, and the factors contributing to the kinetics of the carbon dissolution in these areas, must be understood in order to predict and control how the blast furnace will behave when operating conditions are changed.

Metallurgical coke contains typically 8–12% by mass inorganic mineral matter, derived from the mineral matter found in the parent coals. As coke dissolves in the liquid iron, there is the potential for this inorganic mineral matter to form a layer at the surface of the coke inhibiting the rate of dissolution. This layer cannot be considered solely in terms of a barrier as it is known that inorganic mineral matter itself may be reacting with the carbon and iron. Further, at the dissolution temperatures it can be expected that the nature of the oxide layer will change with composition, mineralogy, temperature and time further complicating the dissolution behaviour of the coke. There is a significant body of research that has focussed on the kinetics of coke dissolution, studying iron melt carbon pick up. Other studies have focused on the reactivity of the inorganic matter, but there are few published data on the nature or growth behaviour of the oxide layer at the interface.

2. Previous Work

The generic term “ash” as used in the ironmaking literature can sometimes be misconstrued as the mineral matter residue from coke combustion, e.g. as determined in the proximate analysis, when in fact it may be a residual product of coke dissolution in iron. In this paper when discussing our results, the inorganic and mineral components of coke will be referred to as mineral matter. To ensure there is no misrepresentation of other researchers work, when referring to their work, the term ash will continue to be used.

Orsten and Oeters using a carburiser cover method, found that there was significant variation in carbon dissolution rate from what was expected following experiments with graphite, and reasoned that during the dissolution of the coke, the ash remaining enriches at the interface. A solid ash product would be distributed over the entire surface, reducing the available contact area between the carbonaceous material and the melt. However, if the ash product was liquid at the melt temperature, it could be flushed away from the interface, reducing this effect.

Gudenau et al. studied the interactions of industrial and special cokes with liquid iron using rotating cylinder method and found that the role of ash was significant in determining the dissolution rate. In this study the authors found that an ash film formed on the surface of some cokes at 1540°C. However, there is no composition provided, nor a detailed description to allow the film to be characterised. This study found that the addition of the refractory oxides, CaO, MgO, Al₂O₃ decreased the dissolution rate while iron oxide enhanced the dissolution rate. SiO₂ was also found to decrease the dissolution rate.

Mourao et al. using a rotating cylinder method, made
similar observations to Orsten and Oeters\textsuperscript{(18)} and Gundenau
\textit{et al.}\textsuperscript{(19)} finding the partially reacted coke sample surface
was porous and covered with a molten slag phase. The
composition of this slag phase was given as 70–90 mass% 
\(\text{Al}_2\text{O}_3\), 6–17 mass% \(\text{SiO}_2\) and 0.3–4 mass% \(\text{CaO}\) with
traces of \(\text{TiO}_2\), \(\text{Na}_2\text{O}\), \(\text{K}_2\text{O}\) and \(\text{P}_2\text{O}_5\) however, the experi-
mental temperature and initial ash composition are not
provided.

Using an experimental procedure that utilised a sessile
drop apparatus to react a drop of iron with a carbonaceous
substrate, Wu\textsuperscript{(16)} and McCarthy\textsuperscript{,5,6)} have reported on the
presence and composition of the ash product at the
melt/carbonaceous material interface.

Wu \textit{et al.}\textsuperscript{(16)} using natural graphite found that although
the carbonaceous substrate contained 8.8 mass% ash, which
was predominately \(\text{SiO}_2\) (72.1 mass%), there was no \(\text{SiO}_2\)
present in the ash on the interface. The ash on the interface
was initially \(\text{Al}_2\text{O}_3\), however as the reaction time increased,
the proportion of \(\text{CaO}\) increased, up to 10 min, after which
the \(\text{Al}_2\text{O}_3\) disappeared and was replaced by a \(\text{Fe}/\text{Ca}/\text{S}
\) complex phase at the interface. The formation of this complex
sulphide was described as the desulphurisation of the metal
drop, however no mechanism for the increasing \(\text{CaO}\) level
or the reduction in \(\text{Al}_2\text{O}_3\) was provided.

Expanding on this work, McCarthy \textit{et al.}\textsuperscript{,5,6)} found that the
carbon transfer between the coke substrate and the
metal drop was influenced by more than the ash fusion
temperature. Reactions between the ash oxides, \(\text{SiO}_2\) and iron
oxides, and the liquid metal could influence the carbon
level in the metal. The formation of the \(\text{Fe}/\text{Ca}/\text{S}\) complex
phase was observed to occur after approximately 30 min of con-
tact time, however the removal of the \(\text{Al}_2\text{O}_3\) from the
surface was not observed. As with Wu’s work, McCarthy
found that there was no \(\text{SiO}_2\) in the ash. This was explained
as the result of direct reduction of \(\text{SiO}_2\) by the solute carbon
from the melt at the interface.

Grigore \textit{et al.}\textsuperscript{(19)} found using XRD analysis of Australian
cokes, that the major mineral phases present were quartz,
mullite and several \(\text{Ca}\) bearing phases, and that a majority
of the mineral matter was contained in an amorphous phase.
The amorphus phase being derived from the decomposition
of the clay minerals during carbonisation and transforming
to an amorphus alumina-silicate glassy phase.\textsuperscript{(20)}

Despite this complex role of the mineral matter at the
interface, there is no published work on the structure of the
mineral matter layer, and work on the composition of the
mineral matter layer is limited to the study of the underside
of iron alloy droplets on a horizontal carbonaceous sub-
strate.

The characteristics of the mineral matter layer are not
well understood. The current knowledge of the mineral
matter layer formed during carbon dissolution is inade-
quate, and can not provide the answer to the simplest char-
acterisation questions such as,
- Is the mineral matter layer solid, liquid or both?
- Does the mineral matter layer have a remanent structure
carried over from the coke, or is the structure different
from the original coke ash structure?
- Is the mineral matter layer porous?
- Does the mineral matter layer accumulate at the interface
or does it break away during the carbon dissolution.

3. Experimental

A series of immersion tests was carried out whereby a
rectangular prism of coke with nominal dimensions of
15 mm×15 mm×40–50 mm (width×thickness×length) was
immersed in a liquid iron–carbon alloy for a period of time,
drop quenched, sectioned and prepared for electro-optical
examination. These experiments were carried in a vertical
tube furnace under a laboratory grade dried argon atmos-
phere with a gas flow rate of 2 L/min maintained through-
out. The temperature was monitored by a Type B \(\text{Pt}/\text{Rh}
\) thermocouple. The furnace had a stable hot zone \(\pm 4\)°C
over a length of 70 mm and \(\pm 10\)°C over a length of
110 mm. Experiments were conducted over the temperature
range of 1 400–1 550°C. The temperature range was chosen
to replicate what might be expected in the lower zone-dead-
man area of a blast furnace.\textsuperscript{,12,11)} A schematic of the furnace
setup and the coke position during the experimental pro-
cedure are given in Fig. 1 and Fig. 2 respectively.

The iron carbon alloy was prepared by melting appropri-
ate amounts of electrolytic iron (\(\approx 180\) g) and spectro-
graphic grade graphite (\(\approx 3.9\) g) to achieve a 2% carbon–
iron alloy prior to dipping the coke sample.

- Coke Sample Preparation and Characterization: The
coke samples used were supplied by BlueScope Steel and
contained approximately 0.4 to 0.45 mass% \(\text{S}\) and
11.6 mass% inorganic mineral matter. The mineral matter
can be considered to be refractory in nature. A detailed
mineral matter composition measured by XRF after ashing
at 815°C is given in Table 1.

The supplied coke was cut into rectangular prisms using
a diamond saw. These were dried in an oven at approxi-
mately 65°C overnight then stored in a desiccator prior to
being loaded into the furnace.

4. Results and Discussion

The reported results are observations and measurements
of the coke–iron interface after quenching. Unless otherwise stated, it is assumed that the results reported and discussed are representative of the high temperature phenomena.

4.1. Observation of the Interface

SEM analysis was performed over large areas of the coke–iron interface. A mineral matter layer was observed at the interface of samples at 1,400°C, 1,450°C and 1,500°C, but due to high magnification required to resolve the mineral matter layer and the large area examined only selected representative images are reported. The coke–iron interface shown in Fig. 3 is typical of the interface at 1,450°C. Though the 1,400°C interface is not shown, Fig. 3 is also typical of the interface observed at 1,400°C.

Typically there was a gap between the mineral matter layer and the coke surface, with the mineral matter layer tending to be found on the metal side of the gap. The profile of the mineral matter layer is usually mirrored by the profile of the coke surface, as shown in Fig. 3, and it is believed that the gap is formed on quenching of the sample as the metal contracts.

The amount of silicon found in the mineral matter layer at the coke–iron interface was significantly lower than that the initial silicon level in the coke mineral matter, as illustrated in the elemental maps (Figs. 4, 5 and 6) and the linescans across the coke-mineral matter-iron interface (Figs. 7(a)–7(c)). There was little or no silicon in the mineral matter at 1,400°C or 1,450°C. Where silicon was found in the mineral matter layer at these temperatures (Fig. 7(b)), it is isolated to the surface adjacent to the coke interface. There is no silicon found on the iron side of the mineral matter layer. The mineral matter layer at 1,500°C contained 8–14 mass% SiO₂. The coke composition moving away from the coke–iron interface was generally depleted in silicon as illustrated in the linescan across the coke–iron interface and into the undissolved coke, Fig. 7(a)).

Sulphur was not found in any of the mineral matter layers at the coke-mineral matter-iron interface. However, as indicated in Fig. 7(d), the presence of sulphur was detected on the iron side of one mineral matter particle that was detached from the interfacial mineral matter layer. This breakaway particle is discussed later.

The coke–iron interface at both 1,400°C and 1,450°C appeared very similar (see Figs. 4 and 5). A continuous band of mineral matter, predominately Al₂O₃, was observed along the coke–iron interface. It was observed to have a
Fig. 4. Micrograph and map of the oxide agglomeration at the coke–iron interface at 1400°C after 20 min of dipping. The scaling bars on the micrographs and maps are 30 and 50 μm respectively.

Fig. 5. Micrograph and map of the oxide agglomeration at the coke–iron interface at 1450°C after 20 min of dipping. The scaling bars on the micrographs and maps are 20 and 50 μm respectively.

Fig. 6. Micrograph and map of the coke–iron interface at 1500°C after 20 min of dipping. The scaling bars on the micrographs and maps are 20 and 50 μm respectively.
thin, ribbon-like appearance, interspersed with large clusters of predominately alumina particles as shown in Fig. 3. The average thickness of the mineral matter layer was determined to be in the order of 6–7 μm. The clusters are an agglomeration of individually distinct angular particles as can be seen in Figs. 4 and 5. The average size of these distinct angular particles was determined using image analysis to be in the order of 1.7 μm while 90% of the particles are less than 4 μm. The distinction between ribbon and agglomeration is an arbitrary one, as both features are comprised of the same particles.

The coke–iron interface at 1 500°C, given in Figs. 6 and 7(a), was observed to have a continuous layer of mineral matter present along the coke–iron interface. The average thickness of this layer was determined to be approximately 8 μm. The structure of mineral matter layer is less angular than at the lower temperatures and individual particles cannot be distinguished.

There is evidence of semi-fused material breaking away from the mineral matter layer at the coke interface. An example of this breakaway material is given in Fig. 7(d). This material appears to be fused and is of the order of
10–20 µm equivalent diameter. There is no evidence of the agglomeration of individual particles that is present at lower temperatures or on the interface at 1 500°C. The iron side of these particles is rounded, indicating melting or fusing at this surface.

At 1 550°C there was little evidence of oxide layer at the coke–iron interface, however there was a slag layer found to have formed on the surface of the liquid iron during the experiment. This slag layer was not observed in the lower temperature experiments.

4.2. Loss of Silicon

The loss of silicon from within the coke and the fact that silicon was not observed in the mineral matter layer are not completely unexpected. There are a number of possible coke reactions that result in the formation of SiO(g) (Eqs. (1) to (4)).

\[
\begin{align*}
\text{SiO}_2(\text{ash}) + \text{CO}(g) &= \text{SiO}(g) + \text{CO}_2(g) \quad \text{(1)} \\
\text{SiO}_2(\text{ash}) + \text{C}(\text{coke}) &= \text{SiO}(g) + \text{CO}(g) \quad \text{(2)} \\
2\text{SiO}_2(\text{ash}) + 3\text{SiC}(\text{ash}) &= 3\text{SiO}(g) + 3\text{CO}(g) \quad \text{(3)} \\
\text{SiC}(\text{ash}) + \text{CO}(g) &= \text{SiO}(g) + 2\text{C}(\text{graphite}) \quad \text{(4)}
\end{align*}
\]

Once this gas is formed, silicon may leave the coke in the gas phase or react with the liquid iron via

\[
\text{SiO}(g) + [\text{C}] = [\text{Si}] + \text{CO}(g)
\]

Generally Eq. (2) would be considered the dominant reaction for SiO(g) generation in a coke sample. Any silica that remains in the coke as the oxide layer is exposed to the carbon containing liquid iron may also be reduced by the iron via

\[
\text{SiO}_2(\text{ash}) + 2[\text{C}] = [\text{Si}] + 2\text{CO}(g)
\]

Loss of silicon from the coke via the gas phase or reaction with the liquid iron has been confirmed by silicon analysis of the iron samples and fume collected on the furnace cap.

4.3. Layer Composition

EDS analysis was conducted on the mineral matter layer either as a point analysis or where possible as an area analysis. The EDS results and associated regions or points in the SEM images are given in Table 2 and Fig. 4, Fig. 5, Fig. 6 and Fig. 7(d) for 1 400°C, 1 450°C, 1 500°C and the breakaway particle at 1 500°C respectively. The compositions in Table 2 are reported as the oxide of the associated element, except sulphur which is reported as calcium sulphide, with an accompanying reduction in the calcium oxide value. Because of the very high background level of iron in the samples, the reported analysis in Table 2 has been normalised to the most prevalent elements excluding iron.

4.4. Layer Formation

Not surprisingly, it has been found that for the coke studied, the form of the mineral matter present at the interface was dependant on temperature. At 1 550°C there was no

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>CaS</th>
<th>Figure Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 400°C</td>
<td>84</td>
<td>*</td>
<td>12</td>
<td>*</td>
<td>Inside boxed area of oxide in Figure 4</td>
</tr>
<tr>
<td>1 450°C</td>
<td>83</td>
<td>*</td>
<td>13</td>
<td>*</td>
<td>Inside boxed area of oxide in Figure 5</td>
</tr>
<tr>
<td>1 500°C</td>
<td>53</td>
<td>14</td>
<td>29</td>
<td>*</td>
<td>Point A &amp; B in Figure 6</td>
</tr>
<tr>
<td>1 500°C (Breakaway Particle)</td>
<td>35</td>
<td>8</td>
<td>29</td>
<td>15</td>
<td>Point C in Figure 7d</td>
</tr>
</tbody>
</table>

*Below the estimated detection limits of EDS (approximately 2 mass%)

mineral matter layer found at the coke–iron interface and a liquid slag had formed on the surface of the melt. At 1 500°C and below a layer of mineral matter material was found at the coke–iron interface.

The temperature dependence of coke dissolution into iron and the effect of mineral matter on the dissolution rate has been subject of many studies. Such studies have generally proposed that solid mineral matter at the interface will reduce the available surface area, retarding the dissolution reaction, and that phases which lower the liquidus temperature of the coke mineral matter, will allow it move away from the interface, and aid the dissolution reaction. However, the work of Orsten and Oetters and recent work from Cham et al. indicate that it is not solely the ash fusion temperature that determines the dissolution kinetics, but the nature of the mineral matter itself plays a significant role in determining the dissolution rate.

To assess the effect of temperature on the equilibrium phase stability of the mineral layer formed in this study a series of thermodynamic calculations using MTDATA were carried out. The compositions used in the calculations were based on the ash components given in Table 1. Only condensed phases in the Al₂O₃–SiO₂–CaO–MgO–Fe₂O₃–Na₂O system (incorporating approximately 96% of listed ash components in Table 1) were considered. The SiO₂ content was stepped from 58.8% mass (as given in Table 1) to half of SiO₂ to quarter of SiO₂ to 0 mass of SiO₂ in Table 1 to replicate the effects of SiO₂ loss from coke. All the Fe₂O₃ was assumed to have been reduced to iron for the lower SiO₂ cases. The oxide compositions were normalised to 100% mass to account for system oxide choice and SiO₂ and Fe₂O₃ removal. The results are given in Figs. 8(a), 8(b), 8(c) and 9(d). The normalised mass% SiO₂ concentrations are 56.9, 42.8, 27.2 and 0 respectively.

Key observations that can be noted from Fig. 8 are that

- An equilibrium liquid phase is predicted for all temperatures and compositions considered containing SiO₂ and that the proportion of liquid oxide increases as the temperature increases.
- No equilibrium liquid phase is predicted across the experimental temperature range for the case simulating complete reduction of the SiO₂ and iron oxides.
- As the SiO₂ concentration of the oxide is lowered there is less liquid phase predicted. The maximum liquid oxide
fraction for the normalised silica masses in the oxides of 56.9, 42.8, 27.2 and 0 are approximately 0.83, 0.55, 0.55 and 0 respectively.

- The primary solid phase changes from the alumino-silicate, mullite (Figs. 8(a), 8(b)) to a mixture of mullite and corundum (Fig. 8(c)) to predominately CA6 (CaO \cdot 6Al2O3) plus a mixture of CA2 (CaO \cdot 2Al2O3), alumina and spinel when no silica is present (Fig. 8(d)).

The thermodynamic calculations make it difficult to conclude that a simple argument based on the liquidus temperature or amount of liquid present is responsible for there being no ash at the coke–iron interface. What is clear though is that if there is SiO2 associated with the oxide then there is the possibility of a significant amount of liquid to be present at the experimental temperatures.

The mineral matter within the coke, is not necessarily combined and locally representative of the bulk composition, instead it may appear as inclusions in the carbon matrix, as single or multiple phase.3,24) Thus in the situation where the silicon, aluminium and calcium were not coincident, it would take a finite amount of time for the oxide components to fuse and approach the equilibrium liquid levels calculated by MTDATA. This fusion process would involve sintering and be complicated by the need for mass transfer of oxide components that are not coincident. Such a process would be temperature activated and expected to be faster at higher temperatures.25) It is likely that a combination of a temperature activated fusion process and its effect on the amount of liquid present in the mineral matter material are critical in determining whether the mineral matter material stays at the coke–iron interface or floats to the melt surface.

The transient effects of silicon loss from the coke further complicate the effects of this fusion process. For a given activity (mineralogy) of SiO2 containing phases and for all other things being equal, it can be expected that increased temperature would increase the rate and the amount of silicon loss to the gas phase.1) Should the activity of the SiO2 be lowered, as would be the case as quartz is taken into solution, or if it reacts with one of the other phases present, then it would be expected that at a given temperature the rate and loss of silicon to the gas phase would be lowered. The dissolution or reaction of quartz (or other siliceous minerals) would be expected to occur during oxide fusion if quartz (or other siliceous minerals) persisted in the coke or oxide layer at the experimental temperatures. Whether this
is a substantive reaction or not would be dependent on the relative rates of SiO$_2$ loss and the fusion process.

A temperature activated fusion process is consistent with the results where the mineral matter layer was observed at the interface. At the lower temperatures of 1 400°C and 1 450°C (see Figs. 4 and 5), the layer of mineral matter material had the appearance of small angular particles of predominately alumina clustered together in ribbons or larger aggregates. It is proposed that the particles that make up these aggregates originate from the mineral matter dispersed throughout the coke, and are exposed, collecting at the interface as the carbonaceous material around the mineral matter is dissolved into the iron. The bulk composition of the mineral matter material found at the interface, given in Table 2, is essentially the same at 1 400°C and 1 450°C, and is very close the composition that would be expected if the mineral matter in the feed coke had the silica and other easily reduced oxides removed. This composition is consistent with the formation of a CA6 phase as predicted by MTDATA at these temperatures in Fig. 8(d) where the silica is removed. However it is evident from Figs. 4 and 5 that the oxide particles maintain a very angular appearance, and a linescan across one of these agglomerations, shown in Fig. 7(b), indicates that the particles are distinct, with compositional differences between the particles making up the aggregate, indicating that equilibrium has not been achieved between the components of the mineral matter.

At the higher temperature of 1 500°C, the bulk composition of the mineral matter material at the coke–iron interface has significant levels of SiO$_2$ (8–14%) that are not seen at lower temperatures. This may be explained by considering the fusion of high activity SiO$_2$ bearing phases with other oxide minerals, lowering the SiO$_2$ activity as discussed previously, resulting in a slower rate of loss of silicon to the gas phase. The greater fusion of the oxide matter shown in Figs. 6, 7(a) and 7(c) is supportive of this. The fusion is also evident in the linescan across the oxide layer shown in Fig. 7(c) where the mineral matter has a consistent composition across the layer, as opposed to the distinct particles at the lower temperatures of 1 450 and 1 400°C. The large agglomerates shown in Fig. 6 are less angular at 1 500°C. It is likely that the more rounded small particles that make up the mineral matter layer at 1 500°C are being softened or were partially molten at some stage due to the compositional changes resulting from the temperature activated fusion process.

### 4.5. Particle Breakaway

The composition and nature of the breakaway particles at 1 500°C shown in Fig. 7(d) deserve particular attention. These rounded, fused particles of mineral material were observed near to the mineral matter layer at the coke–iron interface. It is believed that these particles formed at the interface and either broke away during the coke dissolution process or during quenching. The composition of the breakaway material as given in Table 2, shows that these particles have a very different composition to the original coke mineral matter and are also very different to the mineral matter layer at the coke–iron interface. These particles were observed to have a calcium sulphide layer on the front or metal side. The mass ratio of lime to alumina is in the order of 0.8, therefore it would be expected that a particle would be capable of stabilising a solid sulphur phase or desulphurising the iron melt.

### 4.6. Consequences for Coke Dissolution in Iron

The changes observed in the mineral matter layer at the coke–iron interface at different temperatures may have a significant effect on the coke dissolution kinetics. At 1 550°C there is no mineral matter barrier to inhibit carbon dissolution in iron, therefore coke dissolution will be less hindered. Also when a mineral matter layer is present at the higher temperature (1 500°C) it is likely that the effective porosity will be lower (layer density higher) due to sintering than that of the 1 400 and 1 450°C experiments. Under such conditions it would be expected that the mineral matter layer would provide more resistance to coke dissolution than at 1 400°C and 1 450°C experiments. For all other things being equal, this would result in a slower rate of dissolution of coke in liquid iron. These indications will be studied quantitatively in subsequent work.

### 5. Conclusions

A series of experiments has been carried out in an attempt to characterise the mineral matter layer formed on a coke particle as it dissolves in liquid iron. It was found that

1. The presence of a mineral matter layer at the coke–iron interface was dependant on temperature. At 1 550°C no mineral matter layer was found but in the temperature range 1 400–1 500°C a mineral matter layer was present at the interface.
2. When present, the mineral matter layer formed a continuous band at the coke–iron interface. It had a thin ribbon like appearance interspersed with large alumina or calcium aluminate agglomerates.
3. The large alumina and calcium aluminate agglomerates were composed of smaller particulates.
4. The form of the mineral matter layer seemed to be dependant on temperature. The large alumina or calcium aluminate agglomerates were more angular at lower temperatures suggesting a softening or melting of the smaller particulates at higher temperatures.
5. The temperature dependence of the mineral matter layer formation was explained in terms of a temperature activated time dependant sintering/fusion mechanism and whether the resulting fusion composition contained a significant liquid fraction.
6. There was loss of silicon from the mineral matter in the coke. This was attributed to SiO gas generation and silica reduction by the liquid iron.

### Acknowledgements

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