Significance of Pressure, Temperature and Reaction Rate Events in a Blast Furnace Simulation Test

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1. Introduction

Because of the important effect of the characteristics of the iron-bearing charge on the stability of blast furnace operation, simulation tests are commonly used to assess different charge materials.1–5) These tests employ a profile of temperature and gas composition which is designed to mimic changes experienced by the charge material as it descends through the blast furnace; the sample is also exposed to a compressive load, and molten material which drips from the sample is collected and weighed.

Typical results from such a test are shown in Fig. 1. This figure refers to a REAS 4,5) test result, as studied in this work. The figure shows the way in which the furnace temperature and gas composition were changed; as is typical for these tests, the furnace temperature changed more slowly in the range 900–1000°C, to simulate the thermal reserve zone, and the CO2 content of the gas was gradually reduced to zero. When the sample temperature reached 400°C, the gas was changed from pure nitrogen to a 40% nitrogen mixture (the balance being CO and CO2); the gas was again switched to pure nitrogen once the dripping of the reduced product had started. Specific details of this test are described in the literature,4) and it is sufficient to note here that the sample was contained in a graphite tube of internal diameter 75 mm; the total sample height was 130 mm, made up of a 30 mm coke layer below the iron ore (as used in these tests), and another coke layer above the iron ore. The iron ore sample weighed 0.74 kg and was of the size range 212.5 mm to 10 mm, and the coke layer 10 mm + 8 mm. The gas flowed upwards through the sample, at a constant rate of 0.5 dm3/s (at standard temperature and pressure). The sample was compressed with a dead-weight arrangement, at a pressure of 98 kPa (1 kg/cm2). As Fig. 1 shows, the measured values included the degree of reduction (as deduced from mass spectrometric analysis of the ingoing and outgoing gas), the mass dripped from the sample onto a scale below, the amount by which the sample was compressed during the test, and the pressure drop across the sample.

It is apparent from Fig. 1 that a number of clear events occurs during the test, which have the potential of characterising the behaviour of the iron-bearing material. These events include the sharp increase in pressure (and its subsequent decrease), dripping of molten material (pig iron and slag) from the sample, and arrests in the temperature curve of the sample (the term “temperature arrests” here indicates notable decreases in the sample heating rate which are not simply a result of a slower increase in the furnace temperature).

It has indeed been proposed in the literature that various characteristic temperatures can be derived from these events. These temperatures include the following:

- The first major arrest on the temperature curve is identified as the melting temperature of the slag (TMS).4)
- The last major temperature arrest is identified as the melting temperature of the pig iron product (TMI).4)
- The temperature at which the carbon reaction rate increases substantially (“carbon start temperature” — CST) is taken to indicate the onset of direct reduction.2)
- The temperature at which the gas pressure drop just starts to increase rapidly (T3), the temperature at which the pressure drop reaches a maximum (T9), and the temperature at which the first material drips from the sample (TD)4) are also reported.

While these apparently characteristic temperatures can be determined readily from the experimental results, and have been found to be reproducible for a specific charge
material, it is not clear to which extent the characteristic temperatures do reflect the events which are ascribed to them. For example, what is quoted as the slag melting temperature \((T_{MS})\) is often in the region of 1350°C, which is surprisingly high, given that some fayalite (which already melts below 1200°C) is expected to form during the reduction reactions. For this reason, this work investigated samples from interrupted tests, to determine the condition of the iron-bearing material at different stages (close to the point of maximum pressure). This was combined with a simple energy balance (to investigate the origins of the temperature arrests).

2. Experimental Work

The test conditions were as described above, using lump iron ore. The compositions of the iron ore and coke are given in Table 1. The table illustrates that the ore represents a low-gangue, low-basicity \((i.e.\) low gangue melting point) material. This was a useful property in this investigation, since—if the first temperature arrest does reflect melting of the slag phase—a low gangue melting point should yield a distinct arrest.

Table 1. Chemical composition of charge materials (mass percentages).

| Component | Ore   | Coke Ash |
|-----------|-------|----------|
| Fe₂O₃     | 95.8  | 6.8      |
| FeO       | 0.3   |          |
| SiO₂      | 0.2   | 57.1     |
| Al₂O₃     | 0.98  | 26.9     |
| CaO       | 0.04  | 3.1      |
| MgO       | 0.02  | 1.0      |
| TiO₂      | 0.05  | 1.8      |
| Na₂O      | 0.02  | 0.8      |
| K₂O       | 0.08  | 1.9      |
| P         | 0.04  | 0.12     |
| S         | 0.04  |          |

Note: the coke contained 13.5% ash

Table 2. Test conditions where runs 1 to 3 were terminated.

| Run | Sample temperature (°C) | Pressure drop (mm H₂O) | Percentage reduction | Sample compaction (mm) |
|-----|-------------------------|------------------------|----------------------|------------------------|
| 1   | 1217                    | 152                    | 32.5                 | 25.7                   |
| 2   | 1270                    | 555                    | 38.2                 | 36.8                   |
| 3   | 1316                    | 1204                   | 42.1                 | 47.1                   |

Table 3. Characteristics of other iron sources tested.

| Sample | Iron source | Total gangue content of iron source (mass %) | Gangue basicity (CaO + MgO) / (SiO₂) | Reductant type |
|--------|-------------|---------------------------------------------|--------------------------------------|----------------|
| a)     | Lump ore (higher gangue content) | 9.3 | 0.04 | Coke |
| b)     | 33% Lump ore 1 27% Lump ore 2 40% Sinter | 5.4 | 0.02 | Coke |
|        | 40% Sinter | 9.3 | 0.04 |      |
| c)     | Magnetite pellets | 21.8 | 2.8 | Graphite |
|        |            | 3.2 | 0.33 |      |

To determine the sample conditions at different stages of the test, three interrupted tests were performed. These were terminated at the points marked 1 to 3 in Fig. 1 (spanning the period from the first increase in the pressure drop across the sample, to the maximum pressure). The tests were terminated by flushing the reaction tube with nitrogen, and cooling the sample in the furnace. The conditions where tests 1 to 3 were terminated are listed in Table 2.

The samples were subsequently mounted in resin, polished, and examined in a scanning electron microscope (using backscattered electron imaging to obtain atomic number contrast, and energy dispersive X-ray—EDX—analysis for chemical information).

To test whether the conclusions are more generally applicable, results from other samples were also studied. The characteristics of these samples are listed in Table 3, and the results from their tests given in Fig. 2a) to 2c). The samples mainly differed regarding the type of iron oxide, being lump ore of higher gangue content than that of Fig. 1, magnetite pellets, and an ore-sinter mixture respectively. The masses of the iron source and reductant were also as described in the Introduction.

3. Sample Changes during the Test

The macroscopic appearance of the ore samples following tests 1 to 3 is shown in Fig. 3. The decrease in sample height, loss of porosity, and formation of iron adjacent to the coke layers is evident. Microscopic investigation showed that the samples contained only five major phases:
I) Metallic iron  
II) Wüstite  
III) Fayalite (2FeO·SiO₂)  
IV) Hercynite (FeO·Al₂O₃)  
V) An alkali-rich phase, typically containing 4–6\% (Na₂O+K₂O), 11–17\% Al₂O₃, 25–48\% FeO and 37–53\% SiO₂.

The last two phases (phases IV and V) were quite rare, which is as expected from the low gangue content (see Table 1) of the ore. The typical appearance of four of these phases within the sample is shown in Fig. 4. Hercynite (not shown in this figure) was only observed in isolated regions.

To perform an energy balance on the REAS test, information on the change in the amount of phases with time (and temperature) is required. The phase distribution was calculated from the microscopically observed phases and the chemical analysis of the alkali-rich phase (the other phases were assumed to be stoichiometric); the results are given in Fig. 5. It must be emphasised that the abundances of the phases were determined only to allow the energy bal-
FeO and SiO$_2$ reporting to the alkali-rich phase were deter-
mined, assuming that all Na$_2$O and K$_2$O in the ore report to
the alkali-rich liquid, and in fayalite. Of course, magnetite
does in fact form as an intermediate phase, and metallic
iron forms before all the higher oxides have been reduced
to wüstite, but these changes were found to have an insignifi-
cant effect on the energy balance for a given percentage re-
lance to be performed, rather than to obtain specific mechan-
amic information. This allowed certain simplifications to be
made, which were found not to affect the energy balance,
without probably not being entirely correct as regards the
mechanisms of reduction and slag formation. The calcu-
lated phase distribution is also rendered inaccurate by the
relatively slow cooling of the sample in the furnace, which
allows time for phases to crystallise, with the result that the
observed phase distribution is changed from that at the
peak temperature.

Calculation of the approximate phase distribution pro-
ceeded as follows:

It was assumed that all Fe$_2$O$_3$ is reduced to FeO before
any metallic iron forms. Beyond this time, the assumption
is made that all the iron is present in the form of Fe° and
FeO (the FeO can be present as pure wüstite, as hercynite, in
the alkali-rich liquid, and in fayalite). Of course, magnetite
does in fact form as an intermediate phase, and metallic
iron forms before all the higher oxides have been reduced
to wüstite, but these changes were found to have an insignifi-
cant effect on the energy balance for a given percentage re-
duction. From the average chemical analysis of the alkali-
rich phase (as determined by EDX) the amounts of Al$_2$O$_3$,
FeO and SiO$_2$ reporting to the alkali-rich phase were deter-
mined, assuming that all Na$_2$O and K$_2$O in the ore report to
this phase. The rest of the Al$_2$O$_3$ was taken to be present in
phase IV (hercynite). The balance of the SiO$_2$ (not present
in the alkali-rich phase) was present in fayalite (phase III).
The amount of FeO was then calculated based on the per-
centage reduction, and the amount of pure wüstite was found
as the balance of that not taken up by the alkali-rich liquid,
fayalite-based liquid and hercynite.

The molar percentages (shown in Fig. 5) were calculated
per mole of the relevant compound, i.e. moles of FeO,
Fe$_2$O$_3$, Fe°, hercynite (FeAl$_2$O$_4$), fayalite (Fe$_2$SiO$_4$), and
the total moles of K$_2$O, Na$_2$O, Al$_2$O$_3$, SiO$_2$ and FeO in the alka-
li-based liquid. The slag (assumed to take up all oxides)
was assumed to be molten for temperatures above 1 400°C
(this was based on observation of dripping of slag beyond
this temperature); hercynite and the fayalite are hence as-
sumed to disappear as separate phases as this “dripping”
slag develops. The alkali-rich liquid was assumed to melt
above 980°C, and to be present as a solid (with the same
composition as in test 1) below this temperature. Any pure
FeO was assumed to melt at 1 364°C. Below the tempera-
ture of Test 1, the amounts of hercynite and fayalite (or fay-
alite-based liquid) were assumed to develop, as FeO be-
came available by reduction of Fe$_2$O$_3$. This means that some
unbound SiO$_2$ and Al$_2$O$_3$ were assumed to be present at
lower temperatures, but above 400°C sufficient FeO was
available to form the alkali-rich phase, hercynite and fay-
alite.

4. Energy balance

The rate of heat flow to the sample was found from an
energy balance using the composition of the sample at the
start and end of each time interval (of 30 sec), and the com-
position and rate of the gas flow into and out of the sample.
The data of Kubaschewski et al.31 were used for enthalpies
of the stoichiometric phases. For the non-stoichiometric
phases (alkali-rich phase and slag) the enthalpy correlation
of Turkdogan was employed.32 According to this correla-
tion, the heat of formation of the solid non-stoichiometric
phase at 298 K is given by:

$$H^0_{298} = -285 290 \text{ (J/g · atom)} \quad (1)$$

The increase in enthalpy above 298 K is described by Eq.
(2):

$$H^0_T - H^0_{298} = 5 460 + 49.75T - 6.35 \times 10^{-3}T^2 - 180 \times 10^3 T^{-1}$$
$$-1 110 \sqrt{T} + 1.67 \times 10^{-6}T^3 \text{ (J/g · atom)} \quad (2)$$

where $T$ is in kelvin.

The latent heat of melting of the solid phase is as follows:

$$\Delta H_m = 0.35(H_f^0 - H^0_{298}) - 2 500 \text{ (J/g · atom)} \quad (3)$$

In Eqs. (1) to (3), the enthalpy is given in joule per gram-
atom, i.e. per mole of atoms (Si, K, Na, Fe, Al and O) in the
phase.

5. Discussion

Figure 6 summarises the results of the calculations,
showing 6(a) the rate at which the sample temperature
changed (the differential of the sample temperature curve),
6(b) the rates of reduction and reaction of carbon (as calcu-
lated from the gas compositions), 6(c) the rate of heat trans-
fer to the sample (from the energy balance), and in 6(d) and
6(e) the measured test conditions, together with the calcu-
lated amount of liquid in the sample.

5.1. Pressure Drop

It appears that substantial liquid formation around
1 180°C (melting of fayalite) is associated with the first in-

![Fig. 5. Calculated change in phase abundance, based on the analyses from interrupted tests 1 to 3 (which are marked in the figure). The figures show (a) the main iron-bearing phases, and (b) the main gangue phases, together with the total amount of liquid oxides. Phase abundances are plotted as mole percentages of the total sample.](image-url)
increase in the pressure drop (Fig. 6(d)) (in line with the identification of this temperature as \(T_2\) in the literature, as discussed earlier). However, it does not appear that the subsequent changes in the pressure drop are caused by changes in the amount of liquid present—well past the peak pressure the amount of liquid is calculated to remain unchanged. (Given the uncertainties in the phase calculation, the amount of liquid may well increase slightly, by dissolution of alumina in the fayalite-based melt. However, given the small amount of alumina in the hercynite phase—see Fig. 5—this cannot be a large effect.) The pressure increase rather seems to be associated with substantial compaction of the sample, involving elimination of voids. The different sample types (see Figs. 2 and 6) generally show the first noticeable increase in pressure drop when the sample has been compacted by approximately 30 mm. More compaction than this gives a substantial reduction in sample porosity (see Fig. 3). This is expected to give increased pressure drop across the sample, according to the suggested mechanism that the pressure drop is related to the size of the remaining openings between the particles (the "orifice" model).\(^{9}\) The subsequent increase in pressure drop (with further compaction) is not related in a linear manner to compaction (as the results for the different samples show), but a linear relationship is not expected: compaction results from elimination of both openings between particles and of the porosity that develops within particles during reduction. Only the former is expected to change the pressure drop.

The increased compaction in turn appears to be triggered by increased reduction (Fig. 6(e)). This is in line with the "caving" hypothesis,\(^{10}\) according to which compaction of the burden occurs by elimination of the porosity which forms during reduction. The results in Fig. 6 certainly support this hypothesis, rather than the alternative one that compaction is triggered by liquid formation\(^{10}\)—over the temperature range where compaction occurs, no great change in the amount of liquid is expected, as discussed earlier.

Beyond the peak in the pressure curve, the subsequent decrease in the pressure drop is probably caused by the lowered viscosity of the slag phase at increased temperatures, and a slowing down of sample compaction. The lower slag viscosity presumably allows more (or larger) openings within the sample bed to be opened (by displacement of the liquid by gas), resulting in a lower pressure drop according to the "orifice" model for the pressure drop.\(^{9}\) In addition, above 1370°C the amount of liquid decreases due to the reduction of FeO, which may also contribute to the lowered pressure drop. However, this effect can be of only secondary importance, since it is found well past the peak in the pressure drop (Fig. 6(d)). Similarly, removal of liquid from the sample by "dripping" should also contribute to the pressure decrease. However, Fig. 6 shows that this can only be responsible for the last decrease in the pressure when the sample reaches 1400°C (and dripping occurs)—again well past the peak in the pressure curve.

While the maximum pressure drop is a clearly recognizable event, and one which is assigned to a characteristic temperature (\(T_2\)) in the literature,\(^2\) this does not appear to reflect any particular condition within the sample—the point at which the peak occurs apparently results from a combination of the onset of slower compaction and reduced viscosity. This "characteristic" temperature does not appear to contain information which would be useful in predicting blast furnace stability.

### 5.2. Temperature Arrests

As stated earlier, the first clear arrest on the sample temperature curve is said to indicate melting of the gangue.\(^{41}\) In this sample, such melting occurs just below 1200°C (melting of fayalite; some melting of the alkali-rich phase also occurs at lower temperatures, but this is likely to take place gradually from 980°C onwards, rather than at a single temperature). As Fig. 6(a) indicates, a slight decrease in heating rate is observed at 1200°C, but if the published guidelines are followed,\(^{42}\) this slight arrest would not be identified as the slag melting point—the strong arrest above 1300°C would rather be used (and this reduction in heating rate is even smaller for the other ore types, as shown by Fig. 2). It thus appears that correspondence between the first strong temperature arrest and the "slag melting point" is at best coincidental. Instead, the strong temperature arrest relates to the sharp increase in the reduction rate, and the point
where the carbon reaction rate equals the reduction rate for the first time (i.e. the off-gas contains no CO₂, only CO together with nitrogen). The first strong temperature arrest thus corresponds to the “carbon start temperature” (CST). This is the case for all the samples tested, as illustrated by Fig. 2. Onset of rapid carbon reaction leads to a temperature arrest because of the endothermic nature of the reaction which yields no CO₂ (only CO) as product (see Fig. 6(c)). Identification of the carbon start temperature with the onset of direct reduction does appear justified from the macroscopic appearance of the samples, where the sample from test 3 (terminated at the CST of 1316°C) shows significantly more metallic iron in contact with the coke particles than the sample from test 2 (see Fig. 3).

The second strong temperature arrest (at 1400°C, see Fig. 6(a)) does appear to be associated with melting of the iron phase (TMI), in agreement with the literature suggestion. However, this correspondence is not equally clear for all the samples (see Fig. 2(b) and 2(c)) where two or more arrests follow the first one, and where more than one major dripping event occurs (examination of samples shows that the first dripping event is largely cast iron, and the second slag). These subsequent arrests are sometimes associated with increases in reduction rate (see, for example, Fig. 2(c)) at 1420°C and 1450°C.

It is interesting to note that the lower-temperature arrest (above 1200°C) coincides with a lowering of the reduction rate (Fig. 6(b), and Fig. 2). As suggested in the literature, this is perhaps due to the formation of impervious iron shells around the unreduced cores, by infiltration of liquid fayalite into the porous iron shells around the ore particles.

6. Conclusion

Only in some cases do the “characteristic” temperatures related to blast furnace simulation tests, as cited in the literature, correspond to well-defined conditions within the sample. The first strong temperature arrest does not reflect slag melting, but rather an increased rate of (endothermic) carbon reaction, probably by direct reduction (the “carbon start temperature”). Compaction of the sample and the increased pressure drop across the sample appear to be closely related, and increased compaction seems to be triggered by reduction, according to the “caving” mechanism of softening. The temperature at which the peak pressure occurs does not appear to have fundamental significance. The practical importance of this remains to be tested by comparison with actual blast furnace performance, but it is to be expected that a better understanding of the fundamental origin of test results will allow more successful prediction of the performance of different iron sources in the blast furnace.

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