THERMOCHEMICAL BEHAVIOUR OF OXIDISING SPONGE IRON PELLETS

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ABSTRACT

The effect of the exothermic nature of oxidation on the temperature of oxidising single sponge iron pellets has been examined. The sponge iron pellets employed (produced by reduction in hydrogen at 550°C) were oxidised at 100°C to 400°C.

A mathematical model employing equations involving heat transfer were used to study the thermo-chemical behaviour of the sponge iron during the oxidation process. It was found from this simulation that the temperature predicted to be attainable by the pellets (arising from heat generation) were considerably higher than the nominal oxidation temperatures (i.e. the temperature of the furnace atmosphere) - an indication that the oxidation process was far from being isothermal. The temperatures were also studied by direct experimental measurements. Comparison of the two sets of results indicated that experimental increase in temperature (above the nominal oxidation temperature) was between 60 and 80% of the temperatures predicated by the model. The discrepancies in the result were attributed mainly to heat losses which were not taken into consideration during the experimental measurements. In all the cases investigated overall experimental (or predicted) temperatures during oxidation exceeded 300°C where parabolic oxidation could occur. At higher oxidation temperatures (>250°C), overall temperatures exceeded 450°C where sintering and cavity formation could occur in the sponge iron.

KEYWORDS: *Oxidation, heat transfer, sponge iron pellets, enthalpy.*

INTRODUCTION

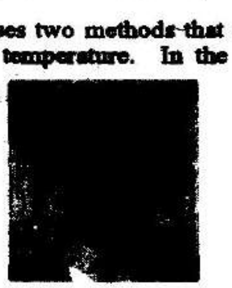
The traditional process of producing iron based on the principle of carbonaceous reduction of iron ores has been unchanged for perhaps 4000 years [1]. This process produces iron through melting of the charge at temperatures in the region of 1400°C, usually in the blast furnace. Although this process is still the cheapest method of producing iron in bulk, capital cost for large blast furnace plants are very high and the metallurgical coke required is not readily available. In many countries a smaller scale alternative to blast furnace, which does not use metallurgical coke is becoming attractive.

The reduction of iron ore pellets using gases such as hydrogen, carbon monoxide, natural gas, etc., at temperatures below the melting point of iron, i.e. 400°C-1100°C, is becoming more and more important. The end product from this process is sponge iron which has a high degree of porosity and is thus far more reactive than iron in its massive state. Oxidation affects the metallization of the sponge iron, especially those produced at lower temperatures. Also, the oxidation process has been observed to be accompanied by heat evolution [2,3,4,5] which further accelerates the oxidation. The presence of moisture may result in the evolution of hydrogen gas which is hazardous.

Some oxidation studies have been carried out on heaps of commercial pellets (reduced at 760°-1100°C) and the effect of the oxidation on the temperature[3]. However, no fundamental work of this nature exists and in any case, sponge iron produced at lower temperatures (<760°C) have not been given much attention. In a previous work [2] involving the oxidation of sponge iron pellets over a range of temperature sintering and cavity formation which are phenomena associated with high temperatures were observed in the microstructures of some of the pellets oxidised at low temperatures. A slight increase in the furnace temperature noted during the oxidation was not sufficient to explain these occurrences. However, considering that the rate as well as the extent of oxidation observed in that work [2] was much more than what was normally observed for iron in its massive state it may be inferred that the oxidation of the sponge iron is likely to be far more exothermic and hence the oxidation process was unlikely to be isothermal as assumed. Any significant rise in the temperature of the pellet during oxidation was likely to affect the reaction rates and the structures of the sponge iron as had been observed.

In order to adequately explain some of the changes observed in the microstructures of the oxidised pellets an idea about the actual temperatures prevailing within the pellets during the oxidation has to be known.

This work discusses two methods that were employed to determine the temperature. In the first method a


Dr. K. Sraku-Lartey

mathematical model developed by the British Steel Corporation (Teesside Laboratories) was employed to predict the temperature in the oxidising pellets. The second method involved direct experimental measurement of the temperatures in the pellet.

BRIEF OUTLINE OF THE MATHEMATICAL MODEL

In an oxidising sponge iron the principles of heat conduction, convection and radiation are of interest. Heat conduction may occur within the solid iron. There may also be heat transfer by convection to a moving gas, or radiation to the walls of the containing vessel or to the bulk gas. The ultimate aim of the model is to estimate the temperature at any position within the pellet at any given time during oxidation.

The main assumptions are as follows:

i) the pellet is considered as a single unit and that oxidation occurs uniformly throughout the pellet,

ii) heat conduction is by Fourier's equation for transient state [6,7],

iii) to obtain the heat generated within the pellet during oxidation, use is made of the variation of rate of oxidation with time obtained in a previous work [2],

iv) heat loss from the surface of the pellet is by radiation and convection.

(a) Heat Generation in The Pellet during Oxidation

The oxidation of the pellets is assumed to proceed according to the reaction:

$$2 \times (3/2Fe + O_2 \longrightarrow 1/2Fe_3O_4)$$

The heat generated per pellet may be obtained from:

$$Q = H.g.d\phi/dt \qquad (1)$$

where $d\phi/dt$ is the rate of oxidation for a pellet in $\%O_2/t$ (see Fig. 1 for the oxidation curves for sponge iron produced at 500°C).

g is the oxygen/iron mole ratio which is equal to (2/3) in this case.

H is the enthalpy of the reaction at nominal oxidation temperatures.

b) Heat conduction in the Pellet during Oxidation

Transfer of heat in the pellet during oxidation is accompanied by heat generation (as discussed in (a)). This is expressed by Fourier's equation as

$$\frac{\delta^2 T}{\delta x^2} + \frac{\delta^2 T}{\delta y^2} + \frac{\delta^2 T}{\delta z^2} + \frac{Q}{k_c}(x,y,z,t,T) = \frac{1}{\alpha}\frac{\delta T}{\delta t} \qquad (2)$$

where, x,y,z are the cartesian coordinates representing a position in the pellet

Q is the heat produced at the position in question

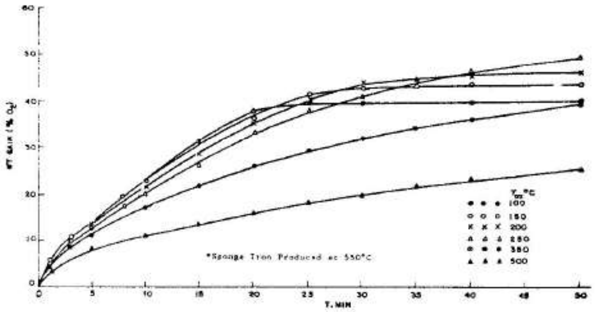


Fig. 1: Oxidation Curves at Varying Oxidation Temperatures (Tox.).

t is time
α is the thermal diffusivity defined as $\alpha = \frac{kc}{\rho Cp}$

where,

kc is the thermal conductivity of sponge iron
Cp is the specific heat of the sponge iron
ρ is the density of the sponge iron

For a spherical particle or solid [where spherical coordinate

$$r = (x^2 + y^2 + z^2)^{1/2} \quad]$$

equation (2) becomes

$$\frac{\delta^2 T}{\delta r^2} + \frac{\delta^2 T}{r\delta r} + \frac{Q}{k_c}(r,t,T) = \frac{1}{\alpha}\frac{\delta T}{\delta t} \qquad (3)$$

where r is the radius of the pellet.

Using Simpson's approximation the expected temperature at a position i after an infinitesimal time Δt is given as:

$$T_{i,j+1} = T_{i,j}\left[1 - \frac{2\alpha\Delta t}{\Delta r^2} - \frac{2\alpha\Delta t}{i\Delta r^2}\right] + T_{i-1,j}.\frac{\alpha\Delta t}{\Delta r^2} + \ldots$$

$$\ldots + T_{i+1,j}.\left(\frac{\alpha\Delta t}{\Delta r^2} + \frac{2\alpha\Delta t}{i\Delta r^2}\right) + \frac{Q}{\rho Cp}.\Delta t \qquad (4)$$

where $T_{i,j} = T(r, t)$

c) **Heat transfer by convection and radiation during the Oxidation**

It was assumed that cooling of the pellet occurred by a combined effect of radiation to the walls of the furnace tube (or gas) and convection by the gas (air) being employed for oxidation.

This is given by

$$h_c(T_s - T_g) + \sigma\varepsilon\,(T^4_s - T^4_w) = -k_c\frac{\delta t}{\delta r} \qquad (5)$$

where,

h_c is the heat transfer coefficient

σ is the Steffan's constant

ε is the emissivity of pellet

T_s is the temperature on the surface of the pellet

T_g is the temperature of the gas (or convective temperature)

T_w is the temperature of the wall of the furnace tube (= Tox, the nominal temperature of oxidation)

d) **Boundary Conditions**

These are;

i. at the centre of the pellet

$$\frac{\delta T}{\delta r} = 0$$

ii. at the surface of the pellet equation (5) holds

RESULTS OBTAINED USING THE MATHEMATICAL MODEL

The results were obtained with assistance from the British Steel Corporation Teesside Laboratories [8] where a computer employing the mathematical model was used to simulate the oxidation process.

Examples of the temperature profiles in some oxidising pellets are shown in Fig. 2-5. The convective temperature (Tg) for Figs. 2 and 3 are equal to the oxidation temperature (T_{ox} = 250°C) whilst for Figs. 4 and 5, T_g was assumed to be 100°C less than the oxidation temperature ($T_g = T_{ox} - 100$). The curves show the temperatures at positions within the pellet of diameter 5.5 mm at varying oxidation times. In the case of Figs. 2 and 4 oxidation was assumed to occur uniformly throughout the outer half of the pellet, the inner core being assumed not to participate in the process. This variation is to cater for a situation where pellet oxidises progressively from the outside towards the interior of the pellet. In this case the evolution of heat towards the outside of the pellet would be high but would be free to escape both into the interior of the pellet and through the outer surface. Figs. 3 and 5 however, show uniform oxidation throughout the pellet as assumed in the model. Here the heat evolved can only escape through the outer surface of the pellet. In the case of the unreacting core, it was assumed that an outer layer of pellet achieved 40% oxidation before oxidation of the adjacent inner layer commenced.

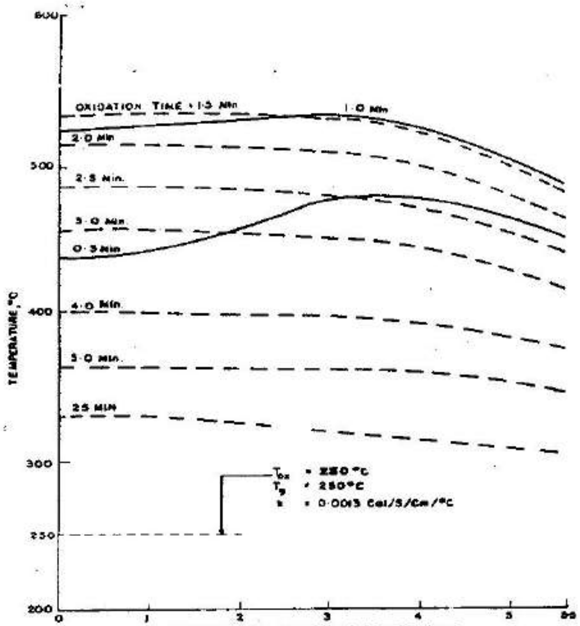


Fig. 2: Change In Temperature Against Time of Oxidation within Pellet (Non-Reacting Core)

In Fig.2, it may be seen that after about 0.5 min of oxidation the temperature has already risen above 400°C, the highest temperature, 480°C, occurring at about 3.5 mm from the centre of the pellet. After 1.0 min the temperature is over 500°C, the highest, 535°C, being 3.0 mm from the centre of the pellet. At this time, the temperature at the centre of the pellet is 525°C, whilst that at the surface is 485°C. After about 1.5 min of oxidation, however, the curve shows that the highest temperature, 535°C, occurs at the centre. This temperature remains constant up to about 3.0 mm from the centre of the pellet, decreasing to 480°C at the surface. From 2 min onwards the temperature throughout the pellet decreases with increasing oxidation time though the centre shows a higher temperature than the other positions in the pellet. After 25 min. the temperature has fallen to 330°C at the centre and 305°C at the surface, both temperatures are, however, still above the nominal oxidation temperature of 250°C.

Fig. 3 also shows the temperature profile in a pellet oxidised at 250°C but where uniform oxidation was assumed throughout the whole pellet. After 0.5 min. of oxidation, the highest temperature, 510°C, occurs at the centre of the pellet instead of nearer the surface as was the case in Fig.2. The temperature decreases from the centre to the surface of the pellet and this profile prevails throughout the oxidation. The highest temperature, 580°C, occurs after 1.0 min. at the centre of the pellet and is higher than the 535°C obtained for the case shown in Fig.2.

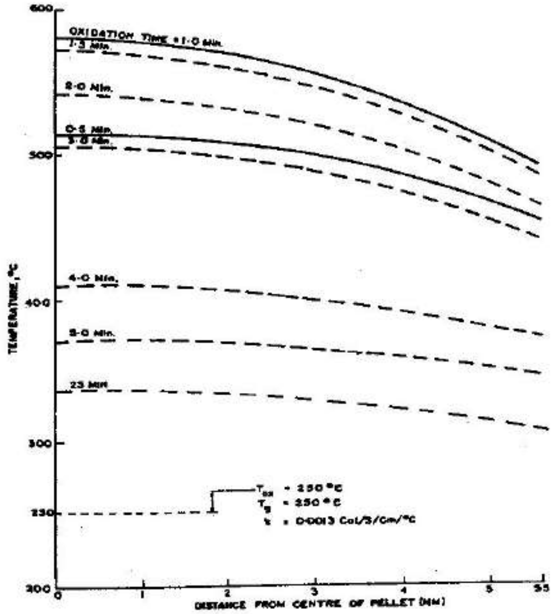


Fig. 3: Change In Temperature Against Time of Oxidation within Pellet (Assuming a Reacting Core)

In addition to whether there is a reacting or non-reacting core, factors such as the thermal conductivity of the iron pellet and the convective temperature, (temperature of gas) were found to affect the temperature of the pellet during the oxidation. These effects are summarised in Table 1 the oxidation being at a nominal temperature of 250°C. The gas temperature was varied from 250°C to 50°C for convection and the thermal conductivity of the sponge iron also varied from 0.0013 to 0.065 cal/cm/sec/deg.C, the figure 0.065 being nearer that of massive iron. In Table 1 only the temperature at the centre (Tc) and surface (Ts) of the pellet are shown. The last two columns show the rise in temperature in the centre (Tc) and the surface (Ts) above the nominal oxidation temperature of 250°C. It may be seen from the figures in these columns that the rise in temperature at the centre is higher where the inner core is reacting (YES). Cases 1 and 2 (and 3 and 4) are typical examples and show that with a reacting core, the temperature at the centre of the pellet is 46°C higher than if the core was not taking part in the oxidation reaction. On the surface of the pellet the difference is only 9°C. The effect of varying the thermal conductivity from 0.0013 to 0.065 cal/cm/sec/deg.C may be seen from cases 4,6,7 and 8. Here, the rise in temperature at

Figs. 4 and 5 show cases where the gas or convective temperature was assumed to be 100°C lower than the oxidation temperature. The major effect here is the lowering of the maximum temperatuges by 10°C.

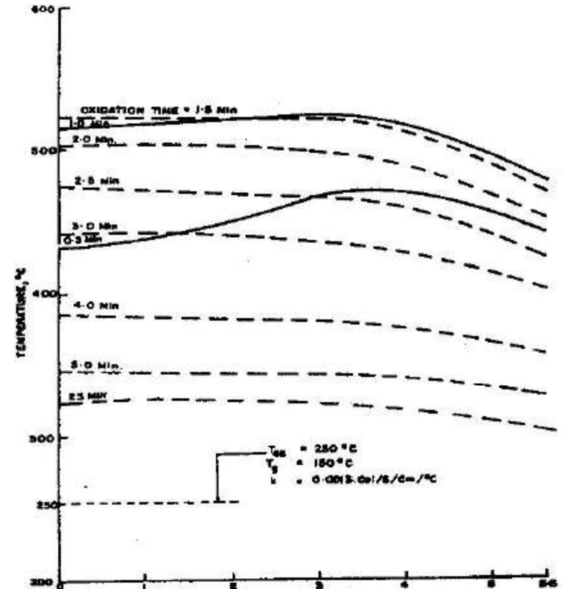


Fig. 4: Change in Temperature Against Time of Oxidation within Pellet (Non-Reacting Core)

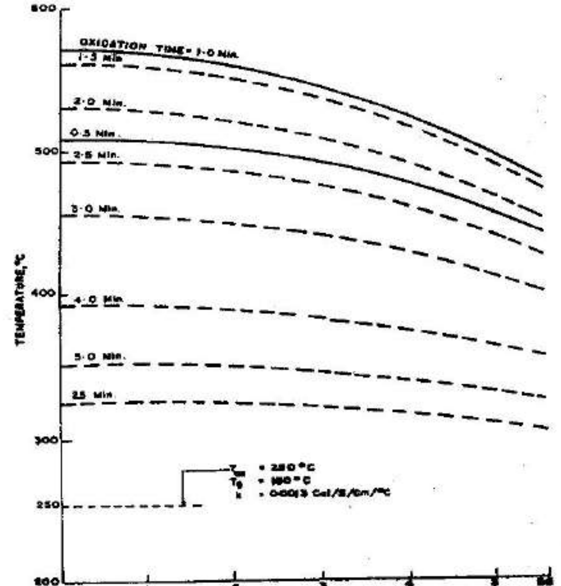


Fig. 5: Change In Temperature Against Time of Oxidation within Pellet (Assuming a Reacting Core)

TABLE 1: EFFECT OF SOME PARAMETERS ON THE TEMPERATURE CHANGES IN OXIDISING SPONGE IRON PELLETS (NOMINAL OXIDATION TEMPERATURE, T_{OX} = 250°C)

Case No.	Gas Temp. T_g, °C	Thermal Conductivity cal/cm/s/°C	Reacting core	Centre Temp T_c,°C	Surface Temp T_s,°C	T_c-T_{ox} ΔT_c,°C	T_s-T_{ox} ΔT_s,°C
1	250	0.0013	NO	535	481	285	231
2	250	0.0013	YES	581	490	331	240
3	150	0.0013	NO	524	470	274	220
4	150	0.0013	YES	571	479	321	229
5	50	0.0013	YES	560	468	310	218
6	150	0.0026	YES	532	484	282	234
7	150	0.0039	YES	518	486	268	236
8	150	0.065	YES	486	484	236	234
9	250	0.0026	NO	518	492	268	242
10	150	0.0026	NO	507	481	257	231

the centre of the pellet decrease from 321°C to 236°C with increasing thermal conductivity. At the surface a slight increase of 5°C occurs in changing the conductivity from 0.0013 to 0.0026 cal/cm/sec/deg.C but thereafter seems to remain constant even when the thermal conductivity is increased to 0.065. Cases 2, 4 and 5 show the effect of changing the temperature of the gas and indicate that decreasing this temperature from 250°C to 50°C causes a decrease in the rise in temperature at the centre from 331°C to 310°C, and 240° to 218°C at the surface.

It may be inferred from the foregoing discussion that the greatest effect on the temperature when oxidation starts is the thermal conductivity of the pellet. The choice of the convective temperature does not seem to be critical since lowering it by 200°C reduces the central temperature by only about 20°C. The presence of an unreacting core also has a considerable effect on the temperature. For radiation the wall temperature was kept constant and equal to the nominal oxidation temperature. Subsequent simulations were carried out using k = 0.0013 cal/s/°C, Tg about 50° to 100°C less than Tox, and assuming a reacting core.

EXPERIMENTAL MEASUREMENT OF TEMPERATURE IN OXIDISING IRON PELLETS

It has been shown in the preceding section using a mathematical model that considerable increase in the oxidation temperature is likely to occur during the oxidation of sponge iron pellets. Owing to the importance of this phenomena regarding its effect on oxidation, it was considered essential to carry out actual experiments to measure directly the temperature changes during oxidation and compare the results with those obtained using the model.

Owing to the small sizes of pellets (11 mm diameter on average), it was proposed to measure the temperatures at the centre and surface of the pellet, leaving the intermediate positions. A hole was drilled to the centre of the pellet and this housed one of the thermocouples. A small shallow groove was made on the surface of the pellet to hold the tip of another thermocouple. The temperature at the two positions in the pellet were continuously recorded during the oxidation. Air was used as oxidant and temperatures from 100 to 400°C employed. Fig.6 shows the temperature - time curves obtained at the centres of the pellets. (The temperature profiles for the surface of the pellets follow similar trends - these are not shown). The curves show that there is a considerable rise in the temperature during the oxidation process. Oxidation at 250°C for example, produced a temperature of about 450°C in the centre of the pellet.

COMPARISON OF PREDICTED WITH MEASURED TEMPERATURE CHANGES IN SOME OXIDISING SPONGE IRON PELLETS

A few temperature-time curves for the predicted (assuming a reacting core) and measured temperature changes at the centres of the pellet are shown in Fig.7. It may be seen from these curves that the predicted temperature-time curves (from the mathematical model) follow the same trend as those for the measured temperature-time curves, the maximum temperature rise also occurring at the same time. The main difference between the two sets of curves is that the predicted rise

TABLE 2: MEASURED AND PREDICTED TEMPERATURE CHANGES AT THE CENTRES AND SURFACE OF OXIDISING SPONGE IRON PELLETS

	measured temperature, °C				predicted temperature, °C					
	$T_c$max	$T_s$max	$T_{max} - T_{ox}$		T_C max	T_s max	$T_{max} - T_{ox}$		$\frac{\Delta T_c \text{ (meas)}}{\Delta T_c \text{ (pred)}}$	$\frac{\Delta T_s \text{ (meas)}}{\Delta T_s \text{ (pred)}}$
T_{ox}			ΔT_C max	ΔT_S max			ΔT_C max	ΔT_S max		
100	347	333	247	233	480	400	380	300	0.65	0.78
150	416	347	266	197	565	465	415	315	0.64	0.63
250	450	390	200	140	570	480	320	230	0.63	0.61
400	547	514	147	114	622	540	222	140	0.66	0.81

in temperature is more rapid and higher than the measured so that a considerable separation between the curves occurs at the initial portions. The two curves however begin to come closer to each other after about 5.0 min of oxidation. For example, for pellets oxidised at 100°C (nominal oxidation temperature), at 1.0 min, the predicted temperature is 470°C whilst the measured is 325°C; at 5.0 min, the predicted temperature is 310°C whilst the measured is 260°C.

The actual temperature (the overall temperature and the increase in temperature) have been summarised in Table 2. These figures represent temperatures obtained at the centres (Tc) and on the surface (Ts) of the pellets. The figures show that for both predicted and measured temperatures, the maximum overall temperature is at least 100°C higher than the nominal oxidation temperature. The highest measured temperature increase was 266°C; (this occurred in a pellet oxidised at 150°C); the highest predicted is 415°C and also occurred in a pellet oxidised at 150°C. In general, the highest increases in temperature occur at the lower nominal oxidation temperatures where the oxidation rates were found to be higher (see Fig.1). In all the cases shown in the Table,

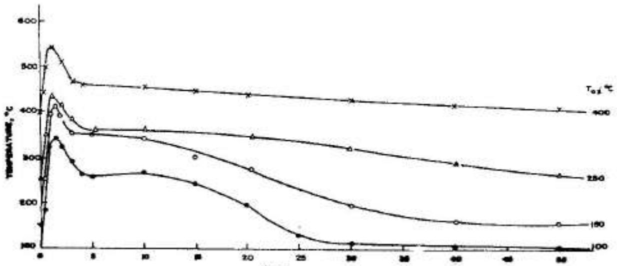


Fig. 6: Measured Temperature - Time Curves Obtained at the Centres of Oxidising Pellets

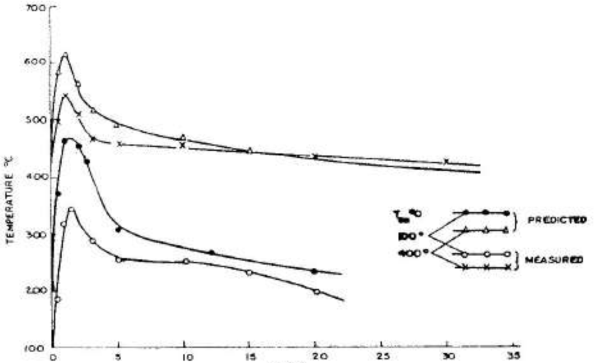


Fig. 7: Predicted and Measured Temperature - Time Curves Obtained at the Centres of Oxidising Pellets

the overall temperature during the oxidation is higher than 300°C, sufficient for parabolic growth to occur in iron. At the higher nominal oxidation temperatures, for example, temperatures above 250°C, the overall temperature in the centre during oxidation increases to at least 440°C and, therefore, within the temperature range where sintering is believed to occur in iron.

The ratios of the measured to the predicted increase in temperature are shown in the last two columns of Table 2 for the centres and surface of the pellets respectively. The measured centre temperature is on the average about 0.65 of the predicted temperature. The measured to predicted ratios for the surface temperatures are similar to those for the centre. That the predicted temperature should be higher than the measured should be expected. The heat losses to the sample container and even the thermocouple sheath would be enough to lower the actual temperature rise that occur during the oxidation and, hence, the measured temperature increase. In both cases several variable factors such as the thermal conductivity of the pellet, the convective and radiative heat, and whether there is a reacting or non-reacting core may affect the rise in temperature. Despite these differences, however, the results show that considerable increase in the temperature occur during oxidation.

SUMMARY AND CONCLUSIONS

The effect of heat generation on the temperature of oxidising sponge iron pellets has been examined. An attempt has been made, using a mathematical model, to predict the temperatures in such pellets. The results obtained are complicated by factors such as the thermal conductivity of the pellet, temperature of the oxidising gas and whether oxidation occurs in the outer parts of the pellets or throughout the pellet. Although predicted time-temperature curves obtained compared favourably with those from measurement of the temperature in the oxidising pellet the measured maximum rise in temperature for the centre and surface of the pellet vary by 60-80% of the predicted values. It must be pointed out that heat losses likely to occur during the experimental work (which would lead to low temperature being recorded) have not been taken into account.

It is clear that some of the control parameters need to be given an indepth appraisal in order to achieve a closer agreement between the two sets of results. It must also be mentioned that bigger size pellets would be easier to handle and therefore enable adequate measurement to be made across the pellet. This work should therefore be taken as a preliminary study of this phenomenon.

Nevertheless, the results obtained seem to explain some of the high temperature phenomenon observed during the oxidation of sponge iron pellets at low nominal temperatures. The evidence indicates that the overall temperatures actually prevailing during the oxidation were higher than the nominal oxidation temperatures. In all cases these exceeded 300°C where parabolic oxidation is likely to occur in iron. In a few cases, the overall temperature exceeded 450°C where sintering and cavity formation are known to occur in iron.

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