Sintering characteristics and kinetics of acidic haematite ore pellets with and without mill scale addition

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Y. Rajshekar[1,2], J. Pal*[1,3] and T. Venugopalan[1,2]

Haematite ore pellets require very high induration temperature (>1573 K) while, magnetite ore pellets require much lower temperature due to the oxidation of magnetite during induration. Mixing of some magnetite in haematite ore can improve the sintering property of pellets during induration. Mill scale is a waste material of steel plant which contains mainly FeO and Fe_3O_4. It can also be blended in haematite ore pellet mix which can enhance diffusion bonding and recrystallisation bonding and facilitate sintering at the lower temperature like magnetite ore. The extent of improvement in sintering property, sintering mechanism and its kinetics in the presence of mill scale is very imperative to study. In current study, the sintering characteristics of acidic iron ore pellet with 15% mill scale and without mill scale has been studied separately through microstructure observation, apparent porosity measurement and volume change. The volume changes due to heating at varying temperature and time has been measured by mercury displacement method and the data has been exploited for sintering kinetics study, wherein, extent of sintering α has a power relation with time. Several kinetics parameters such as time exponent (n), rate constant (k) and activation energies have been estimated for above two pellets and compared. While acidic pellet without mill scale requires 385 k cal mol^{-1}, acidic pellet with 15% mill scale requires only 310 k cal mol^{-1} activation energy.

Keywords: Haematite pellets, Magnetite, Mill scale, Sintering kinetics, Activation energy

Introduction

Green pellet is made from iron ore fines then it is dried and indurated at high temperature to make it sufficiently hard. During high temperature induration the sintering between fine particles in pellet happens through diffusion bonding, recrystallisation or slag bonding. In iron ore pellet, there may be solid state sintering or activated (liquid state) sintering. In a solid state sintering, first neck formation (local bonding) happens between adjacent particles, then pores rounding or pore shrinkage which happens through migration of vacancies, grain boundary diffusion, surface diffusion, plastic flow or condensation of atoms at the surface.[1] This type of shrinkage happens mainly in case of acidic pellet with minor gangue content. In activated sintering the base powder is admixed with the small amount of materials called flux and forms low melting compounds which provide slag bonding.[1] This is happened at the high temperature induration of fluxed iron oxide pellets.

In magnetite ore pellet, oxidation of Fe_3O_4 happens with generation of some exothermic heat (490 kJ kg^{-1}).[2] The oxidation of magnetite helps in diffusion and recrystallisation bonding.[3,4] In contrary haematite pellet has no such oxidation, therefore diffusion or recrystallisation bonding happens at very high temperature and it requires very high induration temperature (>1598 K (>1325°C)) for hardening. Jiang et al.[5] observed that the haematite particles are not enlarged, nor the Fe_2O_3 crystal lattice defects eliminated until the temperature is below 1473 K (1200°C). At higher temperatures, initial connecting bridges are formed between crystal grains and recrystallisation of Fe_2O_3 is observed. Therefore, an acidic haematite pellet requires to heat at very high temperature to form recrystallisation bond (solid state sintering). Otherwise, fluxes are added which enhance activated sintering by the generation of low melting bonding phases.

In order to alleviate the above drawbacks in haematite ore pellet, several investigators[5,6] have mixed magnetite ore powder with haematite ore for enhancing sintering by improving diffusion and recrystallisation bonds. Pal et al.[7] used mill scale as in situ heat source in their pellet-sinter composite agglomerates (PSCA) and found good strength improvement. Mill scale is a waste material of steel plant which is generated in steel mills at the rate of 10–20 kg/ton of crude steel. Since it contains mainly FeO

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Table 1 Chemical composition of iron ore fines and mill scale (wt-%)

	Blaine fineness, $cm^2\,g^{-1}$	Fe_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	P
Noamundi iron ore fines	2200	63.84	0	2.25	2.34	0.001	0.013	0.07
Mill scale	2190	34.32	63.21	0.49	0.28	0.70	0.06	–

and Fe_3O_4, it can also be blended in haematite ore pellet mix which can enhance diffusion bonding and recrystallisation bonding to facilitate sintering at the lower temperature like magnetite ore. The extent of improvement in sintering property and its kinetics in the presence of mill scale is very imperative to study and understand the effect of mill scale on sintering of haematite pellet.

Sintering kinetics of magnetite ore has been studied by Kumar *et al.*[8] through shrinkage measurement method using optical dilatometer. They observed that the rate of sintering is proportional the extent of sintering remaining in pellet. Sintering kinetics of haematite reagent powder has been studied by Wynnyckyj and Fahidy[9] using photographic method and compared the kinetics result with commercial grade oxidised magnetite concentrate. They found higher activation energy for commercial magnetite concentrate than synthetic haematite.

There are advantageous effects of mill scale on sintering but, no study has so far been reported on sintering performance, characteristics and kinetics of mill scale mixed haematite ore pellet. Therefore, in present study, the steel plant's waste, mill scale has been mixed with haematite ore which helps in increasing magnetite content of the mix. Sintering characteristics of mill scale added haematite ore pellet and its kinetics has been studied based on its volume shrinkage during induration. The results have been compared with sintering kinetics of acidic haematite pellet, which help understanding the sintering behaviour and benefits of addition of mill scale in haematite pellet.

Experimental

Haematite iron ore fines of Noamundi, India were taken as the principal raw material and the mill scale was taken from M/s Tata Steel Ltd. The chemical analysis of iron ore fines and mill scale are shown in Table 1. Commercial grade Na-base bentonite was used as binder which contains mainly 45.62% SiO_2, 11.43% Al_2O_3, 12.58%, Fe_2O_3, 1.7% Na_2O and CaO, MgO etc.

First, both iron ore and mill scale were ground in ball mill to make their Blaine fineness of around 2200 $cm^2\,g^{-1}$. 0.5% Bentonite was mixed as binder in a rotary mixer. Acidic pellets were made with and without the addition of mill scale in a disc pelletiser with requisite quantity of water in 2 kg batch. Two types of pellets were made whose blend percentages are presented in Table 2.

The green pellets were subjected to various physical properties. The green compressive strength (GCS) of pellets was measured using a Hounsfield Materials Testing Machine. Green drop strength number (GDSN) was measured by repeatedly dropping a green pellet on a mild steel plate from a height of 450 mm and counted the number of drops that pellet sustains without breakage. The moisture content was measured by heating a representative sample of (25–30 g) at a temperature of 383 K (110°C) for 4 h and subsequently measuring the weight loss in the sample as a percentage. The dry compressive strength (DCS) of the oven dried pellet was done in a Hounsfield Material testing Machine (Model: H10K-S).

The pellets with acceptable green properties were subjected to induration in a muffle type chamber furnace (Molybdenum di-silicide heating element) at varying temperature and retention time. During induration at high temperature the bond formation happens and pellets become sintered. At this stage, the strength of pellets will increase and volume change happens. Two types of heating scheme for the induration were used in this study. One is slow heating of pellet in the chamber furnace (6° C min^{-1}) up to varying set temperature and cooling it in furnace after 15 min of retention to examine the strength property of indurated pellets. This provides an idea on identifying the important temperature range for sintering characteristics and kinetics study in the next step. Other is isothermal heating in the same chamber furnace to study the characteristics and kinetics of sintering which is explained below. Since, the extent of sintering can be measured by volume change, the volume of pellets before and after induration was measured.

The dry pellets bonded with only bentonite forms fines during handling during volume measurement because of its low abrasion resistance. Therefore, the pellets in each batch were coated with a thin film of dextrin solution (7.5% strength) to strengthen the pellet surface. This coating prevented the loss due to wear and tear during volume measurement. The pellets were then kept in open atmosphere under the shade for a day to enable the evaporation of moisture. The volume of pellets was measured by mercury displacement method in a mercury volume metre whose schematic view is shown in Fig. 1. First, the piston was pushed to the extreme end of the cylinder by rotating the gear and the mercury level was adjusted to the zero level by adjusting screw. Then after pulling the piston towards the back, the empty bulb was taken out for sample charging. At least 20 Nos of pellets were taken in each batch and filled inside the bulb. After fixing the bulb, the piston was again pushed to the extreme end of the cylinder and the reading of Hg-level height was recorded which actually indicated the volume of materials

Table 2 Blend percentages of different types of pellets made

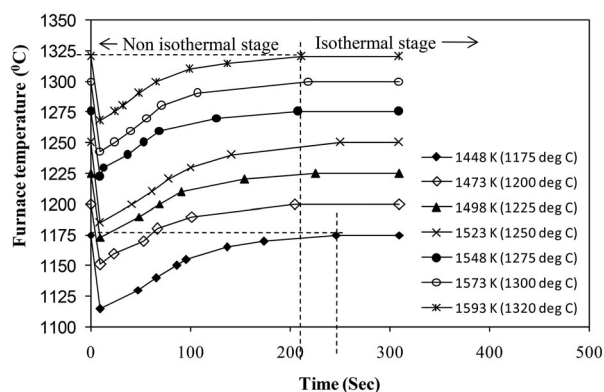| Pellet code	Addition, %			Major constituents, % (estimated)			
	Iron ore	Bentonite	Mill scale	Fe_2O_3	FeO	SiO_2	Al_2O_3
A	99.5	0.5	0	90.87	0	2.46	2.39
B	84.5	0.5	15	82.33	9.48	2.20	2.08
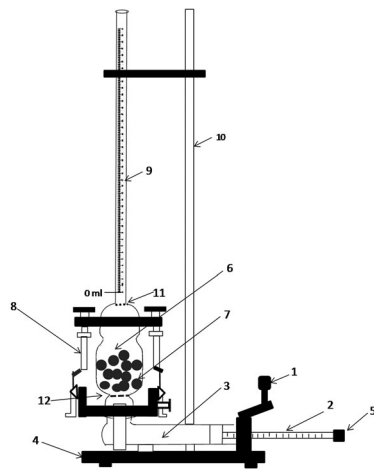
1. Handle with gear, 2. Plunger (piston) with teeth, 3. Mercury chamber, 4. Platform, 5. Screw for zero level setting, 6. Bulb, 7. Pellets, 8. Clamp, 9. measuring column, 10. Stand, 11. Upper grid, 12 Lower grid

1 Schematic diagram of volume measuring apparatus

inside the bulb in cubic centimetre (cc). Thus the volume of dry pellets and volume of pellets after induration was measured and the volume change due to the sintering has been observed.

Each batch of at least 20 Nos of pellet were kept in an inconel crucible which were preheated in an electrical oven at 373 K (100°C) for 2 h and then inserted in an electrically heated chamber furnace (Heating element: Mo-Si_2) for their induration at various temperatures in the range of 1448–1593 K (1175–1320°C) and time intervals. For induration study, the chamber furnace was first heated to a desired temperature of induration and allowed to soak at the set temperature for a period of 20 min for attaining uniformity. Then the furnace door was opened to insert the inconel crucibles filled with pellets for a few seconds and closed immediately. Owing to the opening of the door the furnace temperature was dropped by around 50–60°C and then after closing the gate the temperature was raised gradually to the set temperature by around 3.5–4.0 min. The typical temperature versus time graph for each temperature due to opening and the closing of furnace gate are shown in Fig. 2. Then the pellets were kept in isothermal condition inside the furnace for varying time of retention.

After cooling of the pellets, the shrinkage of the pellets due to the induration at different temperature and time

Table 3   Green and dry properties of pellets

Pellet code	DCS, kg/pellet	GCS, kg/pellets	GDSN
A (acidic iron ore pellet)	9.73	2.1	30
B (acidic iron ore pellet with 1 5 % MS	6.85	2.1	27

was measured by mercury displacement method as explained earlier. Cold compression strength (CCS) of indurated pellets was measured as per standard ISO 4700, using Hounsfield Materials Testing Machine (Model: H10K-S). The Apparent Porosity of indurated pellets was measured as per the standard IS: 1528, part-VIII-1974. The microstructure of chosen pellet samples were observed under an optical microscope (LEICA, DM 2500 M) to examine the extent of sintering in pellets at a particular temperature and time. X-ray diffraction (XRD) analyses of pellets after making powders of it (−100 mesh) were carried out for phase analysis by a Siemens D500 X-ray diffractometer using Cu-K_α radiation. The scanning speed was maintained at 2θ, $1°$ min^{-1}. Phases were analysed by using HighScore Plus (Version: 3.0d) based on Inorganic Crystal Structure Database (ICSD).

Results and discussion

The green properties of both acidic iron ore pellets with 15% mill scale and without mill scale are shown in Table 3. Mill scale added pellets properties are also at par with pure iron ore pellets at the same bentonite content. Mill scale particles have very good wettability and surface smoothness but, only 15% mixing with haematite iron ore does not have much effect on pelletisation property. Thus, both the pellets show good green and dry properties.

Both the pellets were indurated at varying set temperature in a muffle furnace in slow heating scheme and after furnace cooling, the CCS was measured. Effects of induration temperature on CCS of pellets are shown in Fig. 3. The indurated pellet with 15% mill scale shows much higher CCS than without mill scale even at 1373 K (1100°C) and its strength increases with much higher rate. The mill scale added pellet shows more than 225 kg/pellet CCS at only 1473 K (1200°C), while the

2 Temperature change of the furnace after charging of pellet to reach at isothermal condition for different temperature
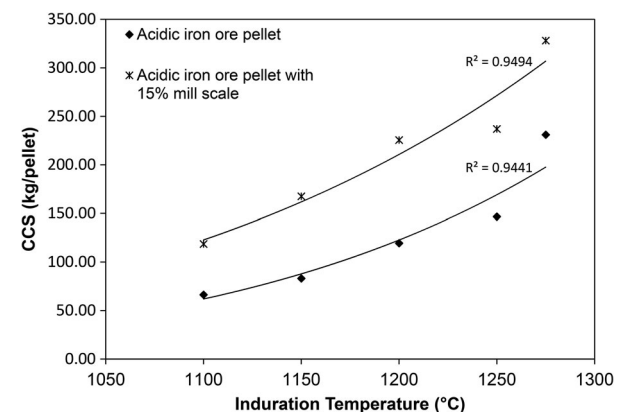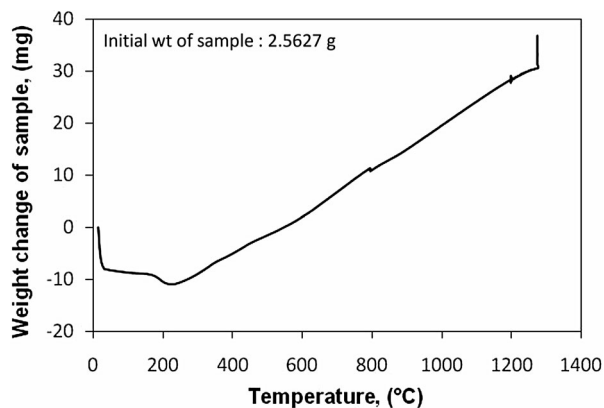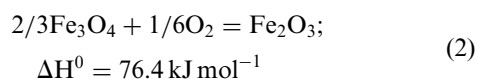

**3 Effect of induration temperature on CCS of pellet**

4 Thermogravimetric analysis of mill scale pellet

pellet without mill scale shows around 120 kg/pellet CCS at the identical temperature. Therefore, there is a substantial increase in CCS due to the addition of mill scale in pellet as mill scale facilitates sintering of fine particles in pellets. As mill scale mainly contains FeO and Fe_3O_4, the oxidation of these oxides during induration at high temperature in air atmosphere takes place which may provide exothermic heat. It may also enhance diffusion bonding favouring diffusion of Fe^{2+} ions towards the reaction interface. The possible reactions are,

$$3FeO + 1/2O_2 = Fe_3O_4; \quad \Delta H^0 = 319.7\,kJ\,mol^{-1} \quad (1)$$

$$2/3Fe_3O_4 + 1/6O_2 = Fe_2O_3;$$
$$\Delta H^0 = 76.4\,kJ\,mol^{-1} \quad (2)$$

The thermogravimetric experiment of mill scale pellet is shown in Fig. 4. The weight gain starts to increase from 473 K (200°C) temperature as above oxidation reactions starts at this temperature and it continues upto high temperature (>1200°C). This is the main reason of better strength development in mill scale added pellet. XRD pattern of indurated (as per slow heating scheme) 15% mill scale added pellet is shown in Fig. 5. Mainly, Fe_2O_3 phase is found without existence of any Fe_3O_4 peaks. However, iron-oxygen equilibrium diagram[10] shows decomposition of Fe_2O_3 to Fe_3O_4 at around 1273 K when oxygen content is reduced below 28 wt-%. However,
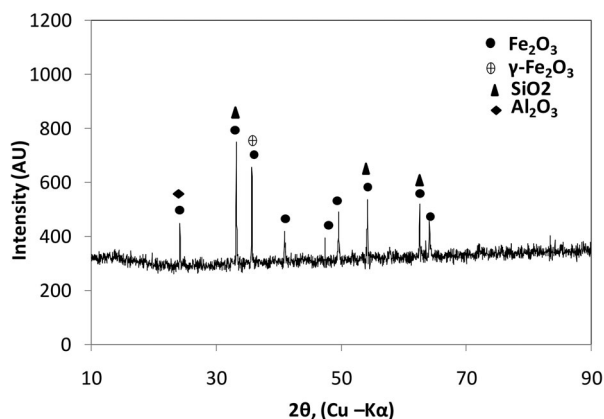
in this investigation FeO/Fe_3O_4 in mill scale becomes oxidised as pellets are heated in air atmosphere. Thus, mainly Fe_2O_3 is found in the XRD pattern. As pellet gets sufficient time in furnace under slow heating and cooling, almost entire FeO/Fe_3O_4 has been oxidised. However, the presence of any minute amount of Fe_3O_4 could not be detected in XRD pattern.

Sintering characteristics

It is evident from the above that mill scale generates *in situ* heat and facilitates diffusion in pellet which enhances solid state sintering. Therefore a comparative study on their sintering characteristics with acidic iron ore pellet is very imperative. In order to study the sintering characteristics of two types of pellets, the pellets (at least 20 Nos) were heated isothermally (Fig. 2) in batches at different temperatures and volume changes were measured as mentioned in the preceding section. It is evident from Fig. 2 that non-isothermal heating time was around 3.5–4 min which is much less than the other reported sintering studies.[8,9] From the above induration study (Fig. 3), it is obvious that acidic pellet with 15% mill scale requires much lower temperature for achieving good CCS than the acidic iron ore pellets without mill scale. Therefore, the isothermal study was carried out at the temperature range of 1448–1523 K (1175–1250°C) for acidic iron ore pellet with mill scale (Pellet B) and 1473–1593 K (1200–1320°C) for acidic iron ore pellets without mill scale (Pellet A). It may be noted that mercury volume metre (Fig. 1) was used for measuring the average volume change of pellets groups due to the sintering at predetermined time. Other investigators used photographic method[9] or optical dilatometer[8] to determine the area of a single pellet during isothermal heating. Although the current measurement process is not continuous measuring during isothermal heating, there are several advantages in it as follows.

(i) While in dilatometric or photographic process measurement is done on a single pellet, the present measurement has been carried out with multiple numbers of pellets (at least 20 Nos) which provides average volume changes of pellets during sintering. Since the sample is commercial grade iron ore and not a pure iron oxide, the average volume change measurement would be more appropriate.

(ii) Direct volume measurement has been done while in dilatometric method the volume change is estimated from the area change or change in diameter.

(iii) Since, both initial and final volume of pellet is measured in cold condition the effect of thermal expansion factor of pellets can be neglected.

Figure 6 shows that the volume reduction during induration happens for both the pellets. The volume reduction increases at higher temperature for both the pellets. However, for mill scale added pellets, the volume reduction is much higher than the pellets without mill scale. The optical microstructures of pellets indurated at 1200°C are shown in Fig. 7. Joining between any two adjacent haematite grains is better in mill scale added pellet. Numbers of pores are also less in mill scale added pellets. This indicates better sintering which may yield decrease in volume of pellets. The microstructures at the

5 XRD pattern of mill scale added (15 wt-%) acidic pellet indurated at 1275°C
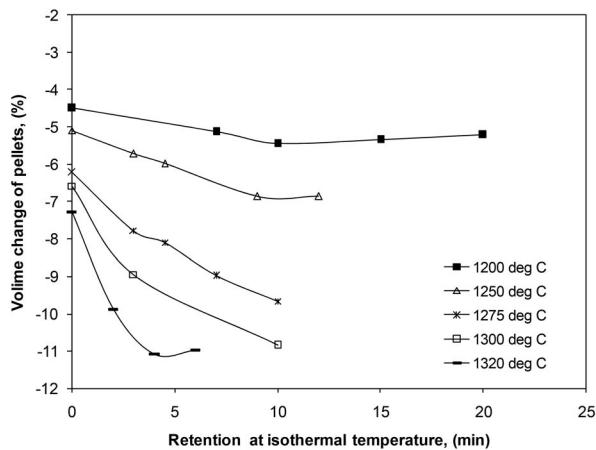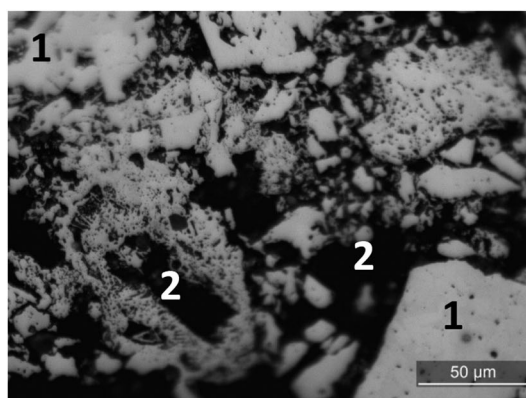
(a) Acidic iron ore pellet
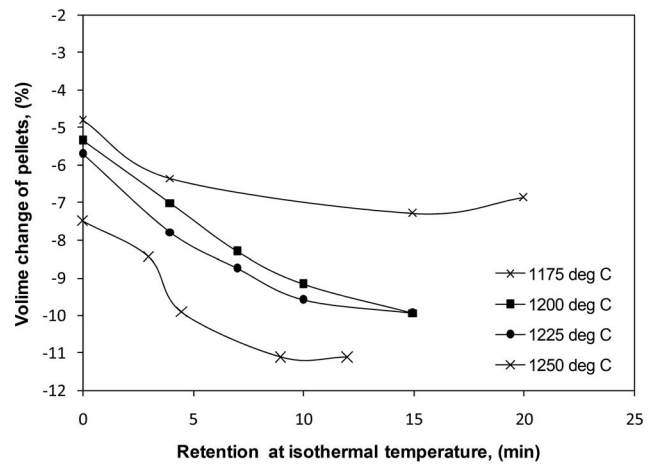
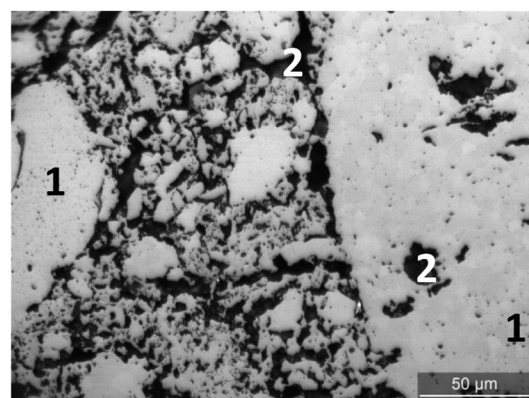(b) Acidic iron ore pellet with 15% mill scale

6 Volume change due to induration at isothermal temperature

edge and centre are also compared in Fig. 8. It is evident from the microstructure that several joining between the adjacent grains are much better in the edge than centre for both the pellets. Especially in the acidic pellets without mill scale, the grains at the centre are separated with black pores and the joining are very negligible and there makes a porous network with connected pores while, in acidic pellets with mill scale, a good amount of sintering has been observed even at the centre. Further, the grey appearance of the grains indicates unoxidised FeO/Fe$_3$O$_4$. Its amount is much higher in the centre than at the periphery. Thus, it is envisaged that sintering of both pellets as well as oxidation of FeO and Fe$_3$O$_4$ in mill scale added pellet takes place from the surface towards the centre. It is depicted from Fig. 6 that the volume decreases with increase in retention time at the isothermal zones also. The optical micro structure in Fig. 9 shows the morphology of mill scale added pellets at the initial stage and after 6 min of isothermal heating. At the initial stage of isothermal heating, the amount of unoxidised FeO/Fe$_3$O$_4$ appears to be much higher which become very low after 6 min of heating. Furthermore, XRD patterns of pellets indurated at varying time are shown in Fig. 10

along with their Rietveld analysis in Table 4. It reveals that during heating in non-isothermal stage, FeO is oxidised to Fe$_3$O$_4$. Further oxidation of Fe$_3$O$_4$ happens during holding it in isothermal condition resulting decrease in Fe$_3$O$_4$ content and increase in haematite percentage. These confirm that FeO/Fe$_3$O$_4$ oxidation happens to be continued during the induration process. However, it has been found by several investigators[11,12] that in pure magnetite pellets at above 1473 K (1200°C), oxidation of Fe$_3$O$_4$ at the core of pellet stops after certain time due to the formation of a ring of impervious sintered haematite. A duplex structure of a haematite shell around the unreacted magnetite core has been found by the above investigators[11,12]. However in current study, this phenomena does not happen and the oxidation of magnetite at the core is also possible which requires some residence time only. This is because mill scale is mixed in a very low proportion (15%) with haematite pellet mix and dispersed in pellet matrix which is oxidised by the diffused oxygen towards the core during sintering. Therefore, FeO oxidation during isothermal sintering throughout the pellet is possible which facilitates sintering. Furthermore, all the phases found in XRD (Fig. 10) have liquidus
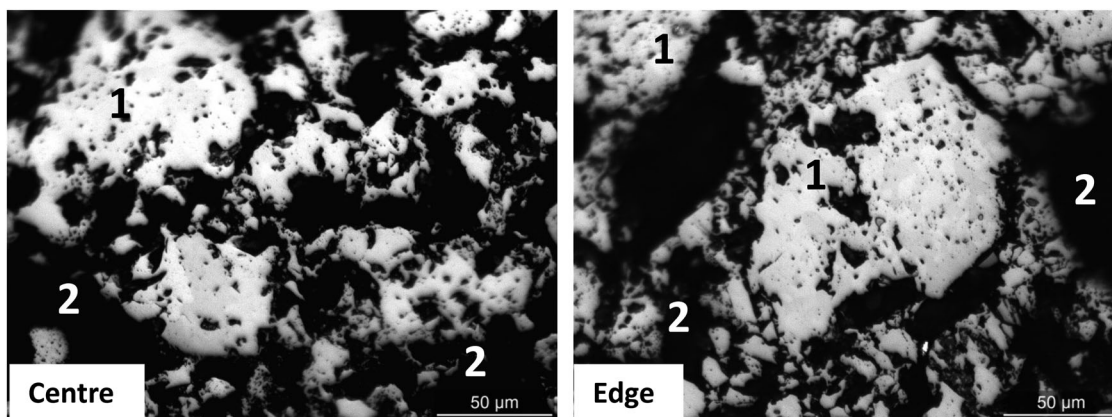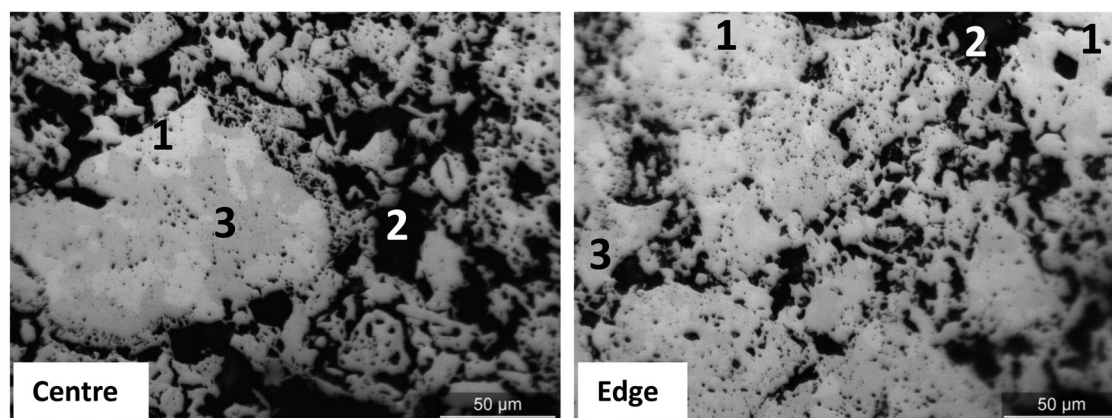

(a) Acidic iron ore pellet

(b) Acidic iron ore + 15% mill scale pellet

1. Hematite (White), 2. Pore (Black)

7 Optical microstructure of pellets indurated at 1200°C for 7 min of holding

(a) Acidic Iron ore pellet

(b) Acidic Iron ore + 15% mill scale pellet

1. Hematite (White), 2. Pore (Black), 3. Magnetite (light grey)

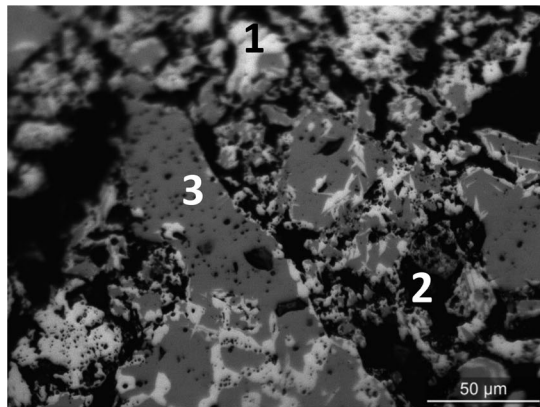**8   Optical microstructure of sintered pellet indurated at 1250°C for 6 min of holding**

temperature above the induration temperature of pellets. FeO may react with SiO_2 in pellet at above 1100°C to form Fe_2SiO_4 but does not react directly with either magnetite or hematite[13]. In this study, FeO present in pellet may be converted to Fe_3O_4 even during heating at the non-isothermal stage due to very fast gas–solid oxidation reaction. Therefore, possibility of low melting Fe_2SiO_4 phase formation is negligible and the present sintering process is considered as solid state sintering. Thus, from the above it is envisaged that (i) FeO oxidation in mill scale added pellets takes place from the surface towards the centre gradually during isothermal heating (ii) sintering in both the pellets also happens from the surface towards the centre gradually during isothermal heating (iii) due to the sintering the volume shrinkage happens in both the pellet.

During induration, the sintering of microparticles happens and thereby porosity of pellet decreases. Therefore, further confirmation on sintering and volume shrinkage was carried out through apparent porosity measurement of isothermally heated samples. Figure 11 indicates that apparent porosity of pellets decreases with increase in isothermal time at any temperature for both the pellets. At higher temperature it decreases to a great extent. Conforming to Johnson[14] densification during sintering takes place when atoms migrate from grain boundaries

to adjacent pore surfaces. During sintering, the bulk density increases, large pore between the adjacent grains decreases in size and grain growth happens resulting densification and shrinkage. The pore shrinkage happens and open pores gradually disappears and the pores starts to be closed by spheroidisation.[15] It is envisaged from Fig. 9 that the decrease in apparent porosity is more in mill scale added acidic pellets than acidic iron ore pellet without mill scale. This decrease in apparent porosity once again indicates the better extent of sintering in mill scale added pellets.

Estimation of kinetic parameters

From the above it is evident that due to isothermal heating, the extent of sintering increases in both the pellets but, higher in mill scale added pellet. However, the rate at which the sintering happens due to the isothermal heating is very imperative to investigate. Rate; i.e. the extent of isothermal sintering in solid state with time has been measured by numerous investigators and found power relation.[16–20] The value of power may vary based on the different mechanisms involves in sintering such as, viscous or plastic flow, evaporation-condensation volume diffusion and surface diffusion etc.[17] Thus, the extent of sintering has power relation with time in isothermal
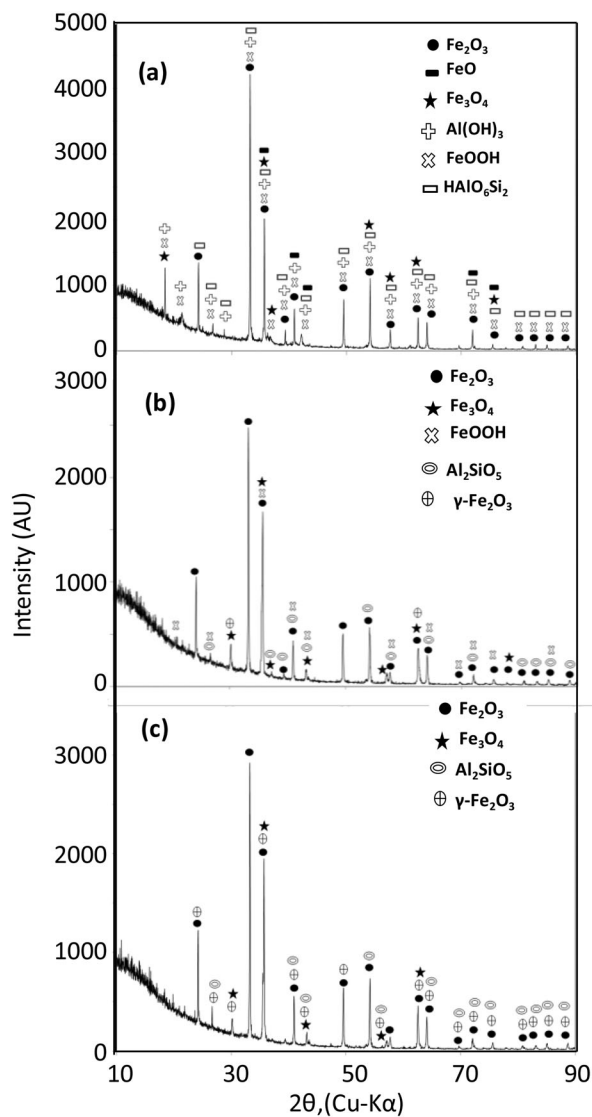
(a) Initial stage of isothermal heating
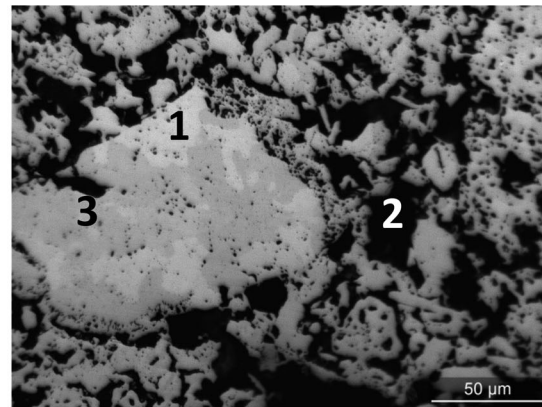
(b) After 6 min of isothermal heating at 1250 °C

1. Hematite (White), 2. Pore (Black), 3. Magnetite (light grey)

9 Optical microstructure of acidic iron ore with15% mill scale pellet at different stages of sintering

(a) Pellet without induration,
(b) Pellet heated in isothermal region to 1200 °C (0 min holding),
(c) Non isothermal heating to 1200 °C plus Isothermal holding for 6 min

10 XRD pattern of 15% mill scale added pellets at different induration condition

condition.[18,19]

$$\alpha = k_1 t^n \qquad (3)$$

k_1 is the coefficient of sintering, t is the time of sintering in s, n is the time exponent which may have different values depending upon mechanism involved and α is the sintering ratio or extent of sintering.

The sintering ratio, α can be defined as the ratio of sintering accomplished to the sintering yet to be accomplished during isothermal heating.

i.e.; $\alpha =$ (Sintering accomplished)/

(Sintering yet to be accomplished) $\qquad (4)$

$$= (V_0 - V)/(V - V_{\text{true}})$$

where $V_0 =$ initial volume of dry pellet before induration, V is the volume of pellet at any instant after certain time of induration and V_{true} is the volume if the pellet undergoes complete sintering with no pore remaining.

Many investigators[8,9] have used this relation (equation (3)) for measuring the sintering rate of magnetite or haematite in solid state. In present study the same relation has been considered with following assumptions.

(i) Isothermal condition was considered based on furnace atmosphere as actual temperature inside pellet during heating could not be measured. Earlier investigators[8,9] also did their kinetics study based on furnace atmosphere.

(ii) Volume change due to magnetite to haematite was neglected. During pure magnetite oxidation to haematite, up to 5% volume increase may be happened.[3] Since mill scale was only 15 wt-% and magnetite content was very low (9.48 wt-%) in pellet, the volume expansion due to oxidation was negligible.

If α^0 is the sintering ratio at the start of isothermal section as demonstrated in Fig. 2, t^0 is the time corresponding to start of isothermal section where pellets attain sintering ratio of α^0,

Equation (3) can be written as

$$\alpha^0 = k_1 (t^0)^n \qquad (5)$$

Table 4 Phases in mill scale added (15%) acidic pellet, estimated from Rietveld analysis of XRD peaks

| Induration condition	Fe_2O_3	FeO	Fe_3O_4	γ-Fe_2O_3	FeOOH	Al_2SiO_5	Al$(OH)_3$	$HAlO_6Si_2$
No induration	69.1	8.1	2.2		13.9		2.5	4.1
At 1200°C in non-isothermal region (0 min holding)	78.3		10.1	5.6	1.8	4.2		
Non-isothermal heating to 1200°C plus Isothermal holding for 6 min	83.1		6.5	4.7		5.7		
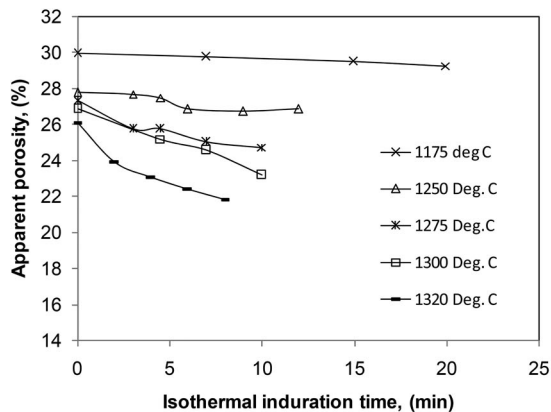
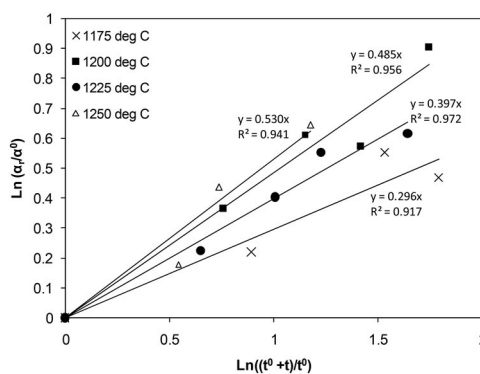(a) Acidic iron ore pellet
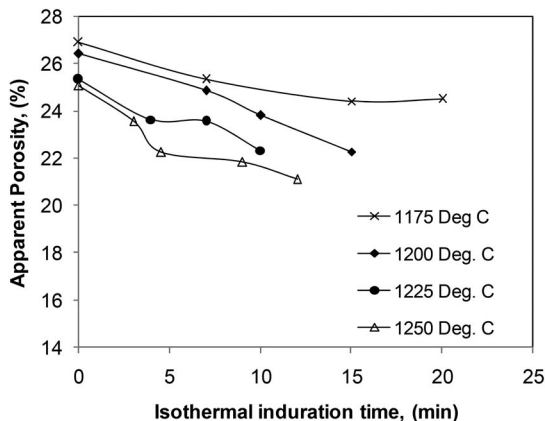
(b) Acidic iron ore pellet with 15% mill scale

11 Effect of isothermal induration on apparent porosity of pellets
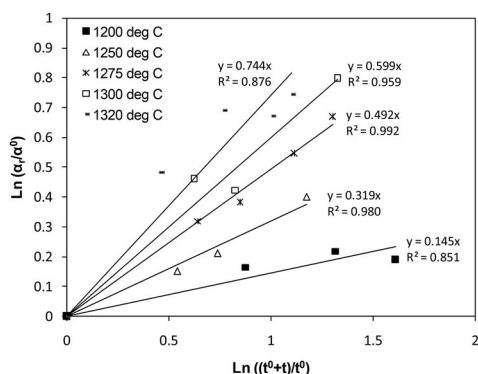
(a) Acidic iron ore pellet

(b) Acidic iron ore pellet with 15% mill scale

12 Logarithmic plots for estimation of time exponent, '*n*'

Consequently, if *t* is the time measured from the start of isothermal section wherein the extent of sintering is α_r,

$$\alpha_r = k_1(t^0 + t)^n \quad (6)$$

Now from equations (5) and (6), it can be written as

$$\text{Ln}(\alpha_r/\alpha^0) = n\text{Ln}((t^0 + t)/t^0) \quad (7)$$

Here t^0 and *t* are measured from the experiments, α^0 and α_r can be calculated from equation (4) using experimental data at the varying temperature and time of sintering. Thus, equation (7) can be plotted for different temperature which may provide straight line and the slope of the lines gives different values of *n* at the different temperatures. The above were calculated with experimental data for the above two materials and the natural log–log plots are shown in Fig. 12*a* and *b*.

The slopes of different lines are indicating the values of *n* at different temperatures. The different values of *n* are summarised in Table 5. The values of *n* are different for the two different materials. It has higher value for the pellet with mill scale than the pellet without mill scale at identical temperature. It is also observed from the table that *n* have increasing trends with temperature which has also been observed by several other investigators[16,21] for other materials too. This is because in the experimental set up the furnace atmosphere is in isothermal condition. However, to achieve isothermal condition in pellet, heat has to be transferred from furnace atmosphere to the pellet core. Higher is the furnace temperature better will be the heat transfer and the sintering will be in faster rate. Therefore, the sintering rate increases with increase in temperature and accordingly the *n* has an increasing trend.

Table 5   Kinetics parameters calculated from equations (3)–(9)

Pellets	Isothermal temperature of sintering, [K(°C)]	Values of 'n'	Values of k, (s^{-1})	Ln (k)	Values of A, (s^{-1})	Activation energy, k cal mol^{-1}
Acidic iron ore pellets	1473 (1200)	0.15	2.9×10^{-7}	−15.0621	2.7×10^{50}	385.2
	1523 (1250)	0.32	4.1×10^{-5}	−10.1034		
	1548 (1275)	0.49	8.9×10^{-4}	−7.0264		
	1573 (1300)	0.60	1.05×10^{-3}	−6.8581		
	1593 (1320)	0.74	5.8×10^{-3}	−5.1478		
Acidic iron ore pellets with 15% mill scale	1448 (1175)	0.29	5.6×10^{-6}	−12.0931	1.5×10^{41}	309.9
	1473 (1200)	0.48	3.6×10^{-5}	−10.2416		
	1498 (1225)	0.40	1.2×10^{-4}	−9.0102		
	1523 (1250)	0.53	1.3×10^{-3}	−6.6415		
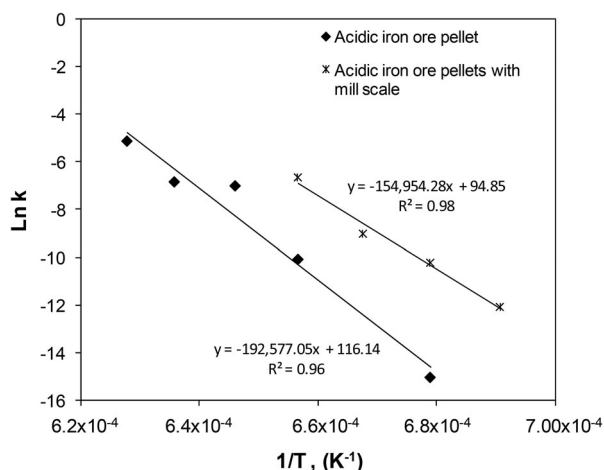
13   Plot of rate constant data in accordance with equation (9) for estimation of activation energy

Now the Arrhenius type equation for the temperature dependence of the rate constant (k) can be written as

$$k = (k_1)^{1/n} = Ae^{(-Q/\mathrm{RT})} \qquad (8)$$

where Q is the activation energy, A is the Arrhenius constant or pre-exponential factor.

Equation (8) can be written as

$$\mathrm{Ln}\ k = \mathrm{Ln}(k_1)^{1/n} = \mathrm{Ln}A - Q/(\mathrm{RT}) \qquad (9)$$

The values of k_1 at the different temperatures in terms of s^{-n} have been calculated from equation [3]. Then the values of k at the different temperatures have been calculated from the values of respective k_1 and n which are shown in Table 5. Accordingly the activation energy of sintering can be calculated from the slope of the plot Ln (k) vs. $1/T$ and the constant A from the intercept of the same plot at 'Y' axis.

The plot Lnk vs. $1/T$ for acidic iron ore pellets and acidic iron ore pellets with 15% mill scale are shown in Fig. 13. Both the plots show straight line with good fitness and from their slopes, the activation energies have been calculated as 385 and 310 k cal mol^{-1}, respectively for acidic iron ore pellets without and with mill scale. The differences in activation energy of the two pellets are mainly due to the presence of magnetite in Pellet B. The difference in size of any material may also be one more reason, however in the present experiment powder size of haematite and mill scale are nearly same (Blaine fineness: ~2200 cm^2 g^{-1}). Although, there may have a slight difference in size distribution, the effect may be considered as negligible.

Thus, this study establishes that mill scale blending in haematite pellet mix help improving the kinetics of sintering during induration and provides better strength properties even at low temperature which intern can reduce the power consumption in induration strand.

Conclusions

(i) Haematite ore pellet requires very high induration temperature (>1573 K). However, use of 15% mill scale in haematite ore pellet provides very good strength even at 1473 K, because of the oxidation of FeO and Fe_3O_4 which facilitates diffusion bonding and recrystallisation.

(ii) FeO oxidation in mill scale added pellets takes place from the surface towards the centre gradually during isothermal heating without forming any duplex structure of magnetite core and haematite shell like magnetite ore pellet.

(iii) Sintering in both the pellets also happens from the surface towards the centre gradually during isothermal heating resulting volume shrinkage and decreasing apparent porosity. However, the amount of volume shrinkage and decreasing porosity is much greater in mill scale added pellet as mill scale facilitate sintering of pellet.

(iv) In the power relation ($\alpha = k_1 t^n$) the time exponent, 'n' has relatively higher value for mill scale added pellet at identical temperature than the pellet without mill scale. Kinetics analysis shows that mill scale added pellet requires much less activation energy (310 k cal mol^{-1}) than acidic iron ore pellet without mill scale (385 k cal mol^{-1}).

(v) Thus, this study provides comparative sintering characteristics and kinetic analysis between acidic iron ore pellets with and without mill scale and proves the application potential of mill scale in haematite ore pellet to reduce the induration temperature which may help to decrease energy consumption.

Acknowledgement

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