Estimation of Sintering Kinetics of Magnetite Pellet Using Optical Dilatometer

T.K. SANDEEP KUMAR, NEELAKANTAN NURNI VISWANATHAN,
HESHAM M. AHMED, CHARLOTTE ANDERSSON, and B. BJÖRKMAN

During induration of magnetite pellets, oxidation of magnetite followed by sintering of the oxidized magnetite (hematite) is desirable. Sintering of magnetite which hampers the oxidation of magnetite is aimed to be kept as low as possible. In succession to our earlier study on sintering behavior of oxidized magnetite (hematite), this paper focusses on the sintering behavior of magnetite phase in isolation with an objective to estimate their kinetic parameters. The pellets prepared from the concentrate of LKAB's mine, which majorly contains (>95 pct) magnetite, are used for the sintering studies. Optical Dilatometer is used to capture the sintering behavior of the magnetite pellet and determine their isothermal kinetics by deducing the three parameters, namely—activation energy (Q), pre-exponential factor (K'), and time exponent (n) with the help of power law and Arrhenius equation. It is interesting to find that the time exponent (n) is decreasing with the increase in sintering temperature. It is also interesting to note that the activation energy for sintering of magnetite pellet shows no single value. From the present investigation, two activation energies—477 kJ/mole [1173 K to 1373 K (900 °C to 1100 °C)] and 148 kJ/mole [1373 K to 1623 K (1100 °C to 1350 °C)]—were deduced for sintering of magnetite, suggesting two different mechanisms operating at lower and other at higher temperatures. The estimated kinetic parameters were used to predict the non-isothermal sintering behavior of magnetite using the sintering kinetic model. Predicted results were validated using experimental data.

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I. INTRODUCTION

IN the prospects of ores getting leaner and finer, pelletization is increasing globally as the most widely practiced agglomeration technique for the ore fines. The major ores being the iron bearing minerals—hematite and magnetite whose fines are being pelletized at large scale across the world. Magnetite ore fines, in particular, have the advantage because of its exothermic oxidation reaction making it more suitable and efficient for

induration subsequent to pelletization. In Sweden, where major source of iron ore is magnetite has developed the expertise in pelletization over the years, as it is the largely practiced agglomeration technique. The blast furnaces in Sweden operate primarily with pellets except for a small proportion of briquettes made out of steel plant solid waste materials.

In pelletization process, magnetite ore is ground and mixed with bentonite as binder then balled in pelletizer to produce green pellets. These green pellets are then heat hardened during induration. Thus, induration is a vital process in pelletization to attain desired pellet quality parameters of strength and reducibility. Induration is carried out either in a straight grate furnace or in a grate kiln furnace. The hot gases are allowed to flow upward as well as downward through the packed bed and in counter-current direction across the furnace for efficient heat transfer. During induration, magnetite pellet undergoes drying, oxidation, and sintering.^[1]

During induration of magnetite pellets, both oxidation and sintering occur. Ideally, it is desirable to have sintering after the complete oxidation of magnetite pellet.^[1,2] In reality, sintering and oxidation may proceed simultaneously. Magnetite sintering will start at a lower temperature than hematite sintering, and remaining magnetite in the core can therefore shrink away from the hematite shell, forming a duplex structure with non-oxidized magnetite core and oxidized shell.^[1,3–7] This is further complicated by the heat generated within the pellet from the exothermic oxidation of magnetite,

T.K. SANDEEP KUMAR, Doctorate Student, is with the Department of Civil, Environmental and Natural Resources (SBN), Lulea University of Technology (LTU), Lulea, 97187 Sweden. Contact e-mail: kamesh.sandeep@ltu.se. NEELAKANTAN NURNI VISWANATHAN, Visiting Professor, is with the Department of Civil, Environmental and Natural Resources (SBN), Lulea University of Technology (LTU), and also Professor, with the Department of Metallurgical Engineering & Materials Science, Indian Institute of Technology Bombay (IITB), Mumbai 400076, India. HESHAM M. AHMED, Assistant Professor, is with the Department of Civil, Environmental and Natural Resources (SBN), Lulea University of Technology (LTU), and also with the Central Metallurgical Research & Development Institute (CMRDI), Cairo, Egypt. CHARLOTTE ANDERSSON, Specialist/Senior Researcher - Oxidation Metallurgy Research & Development, is with the Luossavaara-Kiirunavara Aktiebolag (LKAB), Malmberget, Gällivare, 98381 Sweden. B. BJÖRKMAN, Emeritus Professor, is with the Department of Civil, Environmental and Natural Resources (SBN), Lulea University of Technology (LTU).

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causing sintering of magnetite to occur earlier than otherwise. Therefore, a systematic approach would be to investigate sintering, oxidation, and the heat transfer phenomena independently; the mutual interference of these phenomena can be understood using an appropriate mathematical model at the pellet scale. Further, such a model at the pellet scale can be integrated with models at the reactor scale^[8–13] to predict pellet quality. A collaborative project by Lulea University of Technology (LTU) and Luossavaara-Kiirunavaara AB (LKAB) has been taken up for this purpose. The project has been formulated in parts to study for each of these processes in isolation. The sintering kinetics of oxidized magnetite (hematite) has already been determined in isolation.^[14] The characteristics of magnetite are expected to differ from that of hematite, and hence the focus of the current paper is to independently determine the sintering kinetics of magnetite pellets. The outcome of magnetite sintering along with that of oxidized magnetite (hematite) and their microstructural analysis could be a step toward understanding the overall induration process at pellet scale. This will provide an aid to consider the raw material variability in future (backward integration) and also on the process control parameters to achieve the desired pellet quality (forward integration), and in turn improve the production efficiency. Therefore, it becomes essential to quantify magnetite sintering kinetics in continuation to that of oxidized magnetite sintering kinetics.

Kinetics of process can be evaluated by quantifying them with the three parameters namely—activation energy (Q), pre-exponential factor (K'), and time exponent (n). Sintering kinetics has been studied from the early 1940s quite extensively in the field of powder metallurgy,^[15–25] whereas those of iron ore^[26,27] have been relatively less. It can be noted that unlike conventional powder processing where the objective is to achieve close to complete densification, in iron ore sintering, the objective is to achieve sintering enough to provide sufficient strength during handling and subsequent operation in iron making furnaces. At the same time, sufficient porosity within the pellet is necessary to achieve reduction in least time. In 1974, Wynnckyj and Fahidy made an early attempt by studying the sintering kinetics of pure hematite reagent powder and commercial magnetite concentrate in the form of briquettes under isothermal conditions.^[28] They proposed a power law which relates the extent of sintering with time under isothermal conditions and can be quantified by measuring its shrinkage. Similar approach has been adapted by Kumar *et al.*^[14] recently, wherein shrinkage data of oxidized magnetite are successfully quantified to estimate the above-mentioned three kinetic parameters.

Kumar *et al.*^[14] used Optical Dilatometer as a novel method to measure shrinkage of pellet instead of traditionally used push-rod dilatometer. This new contactless method is also better suited for spherical pellets.^[29] It works on the principle of monitoring the shadow of the pellet sample captured by digital camera equipped with high magnification and long working distance optical systems. It measures the dimensional variations solely on their optical images without having any contact with the sample.

The same approach is now extended to estimate the kinetic parameters by quantifying the sintering phenomena of magnetite. Dimensional changes of a single magnetite pellet (approximately 10 mm diameter) kept in a furnace under argon atmosphere are measured using optical dilatometer to study the sintering behavior of the pellet.

II. EXPERIMENTAL DETAILS

The raw material used was the same concentrate as used in the previously studied hematite sintering.^[14] The concentrate was collected from LKAB's mine in Malmberget, which upon passed by open grinding circuit in ball mills make it suitable for pelletization. The concentrate was targeted to have fineness of 65 pct passing through 45 μm screens and specific surface area $\sim 9900 \text{ cm}^2/\text{cm}^3$ (Blaine No. = 1930 cm^2/gm) measured by Brunauer–Emmett–Teller (BET) Surface Area analyzer. The concentrate having Fe_3O_4 with Al_2O_3 and $\text{SiO}_2 < 0.6$, and 7 pct moisture by weight was mixed, with 0.5 pct dosage of bentonite as binder, in a laboratory mixer (Eirich R02). The chemical analysis of MPC and bentonite is mentioned in Table I.

The mix (7 kg) was then fed to the drum pelletizer (0.8 m diameter) for balling, producing nucleation seeds (3.5 to 5 mm diameter) initially, and then green pellets of desired size fraction (9 to 10 mm diameter) was screened and collected. The desired size here is smaller than the widely practiced industrial average size (10 to 12 mm) of pellets because of the limitations imposed by optical dilatometer on sample size which have been discussed elsewhere.^[14] The green pellets were dried in an oven at 378 K (105 °C) overnight, and stored in a desiccator during the course of the whole project. The pellets were carefully characterized for moisture content, true or skeletal density and bulk density before and after sintering experiments. Moisture content was evaluated by Infrared Moisture Analyzer MA150 (Sartorius AG, Germany) as per the ISO standards. Since the study is focused on single pellet experiments, the surface of the pellet needs to be protected from any contamination to make it suitable for further processing. Therefore, skeletal (true) and envelope (bulk) density of single pellet as a whole were measured by AccuPyc II 1340 (Micromeritics Inc.) and a tailor made Light Table Imaging (LTI) method, respectively, without disrupting the pellet surface. The mean porosity of the pellet was then obtained from their skeletal and envelope densities. Figure 1 shows a schematic of the optical dilatometer used for the study. More details on characterization

Table I. Chemical Composition of Raw Materials

	Concentrate (Wt Pct)	Bentonite (Wt Pct)
Fe	71.06	3.63
SiO_2	0.39	51.64
CaO	0.12	6.43
MgO	0.26	0.68
$\Sigma \text{Na}_2\text{O} + \text{K}_2\text{O}$	0.078	3.30

Fig. 1—Schematic of optical dilatometer (Misura® HSM-ODHT).

Table II. Experimental Design to Study Sintering Kinetics of Magnetite Pellets

Pellet	Sintering Temperature [K (°C)]	Isothermal Time (Min)
P1	1173 (900)	90
P2	1223 (950)	60
P3	1248 (975)	60
P4	1273 (1000)	60
P5	1298 (1025)	60
P6	1323 (1050)	60
P7	1373 (1100)	40
P8	1423 (1150)	40
P9	1473 (1200)	20
P10	1523 (1250)	20
P11	1573 (1300)	20
P12	1623 (1350)	20

methodology and experimental set can be found elsewhere.^[14]

Magnetite green pellets in all the experiments were exposed to the thermal profile from room temperature to desired sintering temperature at a heating rate of 30 K/minute (30 °C/minute), held isothermally for 20 to 90 minutes and then allowed to be furnace cooled. The isothermal holding time was chosen so as to have adequate residence time for sintering to occur. The experiments designed for magnetite sintering studies in isolation are mentioned in Table II. The experiments were designed with temperature intervals of 50 K (50 °C) at higher temperatures [above 1323 K (1050 °C)] and 25 K (25 °C) at lower temperatures with an effort to capture the small dimensional changes.

A single magnetite pellet was kept under inert atmosphere to minimize its oxidation. A constant flow of argon (99.995 pct) gas at the maximum allowable flow rate of $8.33 \times 10^{-6} \text{ m}^3/\text{second}$ (0.5 L/minute) was used to have inert atmosphere across the pellet in the furnace. Higher flow rate of argon is maintained to keep positive pressure inside the furnace all the time to avoid any air infringement into the furnace which otherwise may lead to substantial oxidation. In order to confirm this, sintered magnetite pellets were ground and analyzed with X-ray diffraction (XRD) with a copper target and they were also investigated with light optical microscopy (LOM). The shadow images of the pellet

were captured continuously by optical dilatometer at an interval of 15 seconds to observe the shrinkage during sintering.

III. RESULTS

A. XRD and Microstructures

The XRD patterns for raw material (magnetite concentrate) and pellet exposed to the highest sintering temperature [1623 K (1350 °C)] are shown in Figure 2, where major magnetite peaks (96-900-5814) were found (without those of hematite). The hematite reference (96-901-4881) peak positions are also indicated in the figure. Similar diffractograms with magnetite peaks have been observed for all pellets with sintering temperatures varying from 1173 K to 1573 K (900 °C to 1300 °C). The microstructure of a 10 mm diameter fired magnetite pellet is shown in Figure 3 with focus on its rim. It is observed that there are traces of oxidation at the rim of the magnetite pellet. The maximum thickness of the spread of these traces is approximately 50 to 70 μm . Assuming that the oxidation layer is concentric, the degree of oxidation calculated is found to be less than 4.2 pct. Since, this is such a small percentage and that too at the surface, it is not expected to interfere or have significant effect on sintering of magnetite pellet.

B. Sintering Degree and Its Rate

The typical plot resulting from the sintering of magnetite from the optical dilatometer is shown in Figure 4, where the percentage change in area ($\delta_{A,\text{overall}}$) of a pellet is plotted against time for the given thermal profile.

$$\delta_{A,\text{overall}} = \frac{A - A_0}{A_0} \times 100 \quad [1]$$

where 'A' refers to the projected area of the pellet at any instant of time and ' A_0 ' refers to that at the start of the experiment. Experiments have been repeated with same thermal profile to ensure the reproducibility of the results which is quite good as depicted in Figure 4, and only one of them is plotted further for brevity. However, experiments were repeated for all thermal profiles. The reproducibility of these

Fig. 2—XRD peaks of magnetite concentrate and pellet exposed to highest sintering temperature [1623 K (1350 °C)].

Fig. 3—Light optical ((polarized) microstructure of a 10 mm diameter exposed to sintering temperature of 1423 K (1200 °C) (a) with focus on rim and (b) the overview of whole pellet.

experiments is good considering the fact that pellet to pellet variation in porosity and bulk density is expected. The temperature within the pellet is assumed to be uniform as it is observed from the preliminary confirmatory experiments, and well supported by analytical heat transfer calculations.^[30]

Figure 4 shows that initially the pellet expands thermally, and shrinks later due to sintering at higher temperatures [>1223 K (950 °C)] and thermal contraction during cooling.^[14,31] Thus, the overall change in size of pellet is due to the combination of thermal expansion/contraction and the sintering phenomena. Isolating

the linear thermal expansion/contraction from the overall percentage change in area by plotting it as the function of temperature (see Figure 5), and equating their similar slopes yields the shrinkage of pellet due to sintering alone. The authors could not specifically found the reason for the noise in area change measurement at the start of experiments, but can be attributed to stabilization of images capturing by the software for analysis. Since the percentage change in area is measured from optical dilatometer, volumetric thermal coefficient of expansion (α) is related to its area thermal coefficient of expansion (β), and is expressed in

Fig. 4—Typical plot obtained from optical dilatometer for percent area change with time.

Fig. 5—Area change for magnetite pellets during sintering at different temperatures.

Eq. [2].^[14,32] The values of thermal expansion estimated are comparable with that obtained in the literature.^[33,34]

$$\beta = \frac{1}{A} \frac{dA}{dT} = \frac{2}{3} \alpha \quad [2]$$

Subsequently, the area change due to sintering alone is used for further analysis.

Sintering is a temperature dependent process, and the degree of sintering increases with increase in temperature for magnetite pellets. This is also evident from the micrographs of fired magnetite pellets shown in Figure 6, where grains come closer to each other at lower temperature [1273 K (1000 °C)], form the neck while sintering progresses with increase in temperature [1473 K (1200 °C)], and agglomerated at higher temperatures [1573 K (1300 °C)].

Sintering rate describes the progress of sintering, and is quantified as the degree of sintering (percentage of area change) achieved per unit time during the course of

induration. The relation between the sintering rate of magnetite pellet and sintering temperature is shown in Figure 7. It shows that the sintering rate increases in the non-isothermal segment whereas it decreases with time in the isothermal segment. This is because the driving force for sintering, the surface area of grains in the pellet (pore surface area), decreases with the extent of sintering.

C. Sintering Ratio (γ)

Sintering ratio for the pellet is defined as the ratio of the sintering accomplished to the sintering yet to be accomplished as expressed in Eq. [3]. In 1974, Wynnickyj and Fahidy^[28] have suggested that this sintering ratio can be a measure to quantify sintering of pellets by capturing their shrinkage. In the preceding study, Kumar *et al.*^[14] have successfully quantified the sintering of oxidized magnetite (hematite) pellets with a similar approach. Thus, in this study, the same approach has now been extended to quantify the sintering of magnetite pellets.

$$\gamma = \frac{\text{Sintering accomplished}}{\text{Sintering yet to be accomplished}} = \frac{V_0 - V}{V - V_{\text{true}}} \quad [3]$$

where V_0 is the initial volume of the pellet, V is the volume of the pellet at any instant during sintering and V_{true} is the volume if the pellet would have undergone complete sintering with no pores remaining. Since only the change in area of pellet during sintering is measured, it needs to be related to the sintering ratio of pellets. Bulk density and true density of pellets measured by LTI and Helium pycnometer, respectively, are used and rearranged to obtain an expression for sintering ratio in terms of area change due to sintering.

$$\gamma = \frac{-\delta_{A,\text{sintering}}}{\delta_{A,\text{true}} + \delta_{A,\text{sintering}}} \quad [4]$$

where $\delta_{A,\text{sintering}}$ is the area change at any instant during sintering and $\delta_{A,\text{true}}$ is the area change if the pellet would have sintered with zero porosity. This sintering ratio (extent of sintering) is shown in Figure 8. It is plotted against time for pellets exposed to different isothermal temperatures and further used for determination of kinetics.

D. Sintering Kinetics

Sintering of magnetite pellets is quantified by determining the aforementioned three basic kinetic parameters—time exponent, activation energy, and rate constant. The isothermal sintering time (t) of the reaction (assuming two-sphere particle model) is related to the extent of sintering (γ) with a time exponent (n), as expressed in Eq. [5].^[14,28] The time exponent of the reaction determines the reaction mechanisms which are dominant during sintering of pellet at various stages as it progresses.

$$\gamma = Kt^n \quad [5]$$

Fig. 6—Optical microstructures of fired magnetite pellet at 1273 K, 1473 K, and 1573 K (1000 °C, 1200 °C, and 1300 °C), at magnification of 200 times.

Fig. 7—Sintering rate of a magnetite pellet for a given thermal profile.

where K is the rate constant. Further, this reaction constant term can be related to temperature with an Arrhenius form of expression (Eq. [6]).

$$\ln(TK^{(1/n)}) = \ln K' - \frac{Q}{RT} \quad [6]$$

where Q is the activation energy and K' is the pre-exponential factor.

Fig. 8—Sintering ratio for magnetite pellets during sintering at different temperatures.

The isothermal segment of sintering ratio curves (Figure 8) is used to estimate the sintering kinetic parameters. The sintering ratios of the pellet at the beginning and at any instant of isothermal sintering have been compared according to Eq. [5] giving the following expression,

$$\ln\left(\frac{\gamma}{\gamma^*}\right) = n \ln \frac{t^* + t_m}{t^*} \quad [7]$$

where γ^* is the sintering ratio at the start of the isothermal section, t^* corresponds to a time if the pellet had attained a sintering ratio of γ^* from the start under isothermal condition, and t_m is the measured time from the beginning to any instant of isothermal section corresponding to sintering ratio γ , as shown in Figure 9. The parameters n and t^* were estimated using least square fit for experiments at different sintering temperatures for magnetite pellets, and has been plotted as shown in Figure 10.

Please note that linearity of points ($R^2 > 0.975$ and $\sigma < 0.04$) at different temperatures in Figure 10 confirms the validity of Eq. [5] in describing the sintering kinetics. However, it can be observed that at lower temperatures, there are significant fluctuations about the straight line whereas at higher temperatures the fluctuations are much less. This might corresponds to the fact

Fig. 9—Depiction of parameters of power law from sintering ratio plots with respect to time.

Fig. 10—Time exponent ‘ n ’ estimated from the slope of curves, for magnetite pellets sintered at different temperatures.

that at lower temperatures the shape of the pellet, as well as variation in shape and packing of grains in the pellet, may be influencing the initial sintering phenomena. These fluctuations might also be attributed to the fact that the shrinkage values are so small at low temperatures that there might be uncertainties in the measurements.

Ideally, all the points in Figure 10 would have fallen on one line, for a single value of n , as suggested by Eq. [6]. However, the present results show a variation in the slope, ‘ n ,’ for different sintering temperatures, as tabulated in Table III.

In order to explore further, the exponent ‘ n ’ was plotted as a function of temperature as shown in Figure 11. The value of ‘ n ’ varies from 0.45 to 0.15 in the range of temperatures from at 1173 K to 1623 K (900 °C to 1350 °C). A linear fit for predicting n as a function of temperature (with two data points considered as outliers) is given by

$$n = -4 \times 10^{-4}T + 0.72 \quad [8]$$

Further, from the variation of sintering ratio, γ , with time, t , in the isothermal section the values of sintering rate constant, K , in Eq. [5] for different temperatures is estimated knowing respective γ^* , t^* , and n . In order to estimate the activation energy, Q and the pre-exponential factor, K' , $\ln(KT^{1/n})$ is plotted as a function $1/T$ as shown in Figure 12. Two separate lines can be inferred from the plot, as illustrated in Figure 12. Corresponding to these lines, the ranges of temperatures, activation energies Q_1 and Q_2 , and the pre-exponential factors K'_1 and K'_2 are shown in Table III.

The activation energies for magnetite pellet sintering at lower temperatures are higher than at higher temperatures suggesting different sintering mechanisms at lower and higher temperatures.

E. Sintering Prediction

In order to simulate the actual industrial process where sintering occurs under non-isothermal conditions, the estimated kinetic parameters determined for isothermal magnetite sintering by Eqs. [6 through 8] are further extended to non-isothermal sintering by similar approach which had been adapted for the sintering of oxidized magnetite.^[14] The care has been taken to incorporate the variation of ‘ n ’ with temperature and also the two activation energies while marching in time for sufficiently small step of Δt (discretized time – temperature plot) to generate the profile for sintering ratios as expressed in Eq. [9].

$$\gamma_{t+\Delta t} = K(T_{t+\Delta t}) \left(\left(\frac{\gamma_t}{K(T_{t+\Delta t})} \right)^{1/n} + \Delta t \right)^n \quad [9]$$

where γ_t and $\gamma_{t+\Delta t}$ denote the sintering ratios at time t and $t + \Delta t$, respectively, and corresponding temperatures be denoted by T_t and $T_{t+\Delta t}$, and $\left(\frac{\gamma_t}{K(T_{t+\Delta t})} \right)^{1/n}$ is the time that would have taken to achieve sintering ratio of γ_t isothermally at temperature $T_{t+\Delta t}$.

Table III. Kinetic Parameters for Sintering of Magnetite Pellets

Sintering Temp. [K (°C)]	n	$K (\times 10^{-3}) (s^{-1})$	$t^* (s)$	Activation Energy (kJ/mole)	Pre-exponential Factor (K/s)
1173 (900)	0.35	8.2	953.81	$Q_2 = 477$ kJ/mole [1173 K to 1373 K (900 °C to 1100 °C)]	$K'_2 = 3.66 \times 10^{14}$ [1173 K to 1373 K (900 °C to 1100 °C)]
1223 (950)	0.31	1.6	832.86		
1248 (975)	0.20	6.1	192.20		
1273 (1000)	0.44	1.1	849.93		
1298 (1025)	0.25	6.9	242.56		
1323 (1050)	0.35	3.7	533.74	$Q_1 = 148$ kJ/mole [1373 K to 1623 K (1100 °C to 1350 °C)]	$K'_1 = 3.51 \times 10^2$ (1373 K to 1623 K (1100 °C to 1350 °C))
1373 (1100)	0.33	7.8	412.57		
1423 (1150)	0.30	17.4	367.82		
1473 (1200)	0.25	27.9	351.66		
1523 (1250)	0.22	39.9	474.17		
1573 (1300)	0.20	58.5	471.17		
1623 (1350)	0.15	141.3	217.95

Fig. 11—Variation of time exponent ' n ' for pellets exposed to different sintering temperatures.

For the purpose of validating the sintering profiles predicted by Eq. [9], experiments have also been performed with pellets exposed to three different heating rates up to a temperature of 1573 K (1300 °C) in optical dilatometer, and are compared in Figure 13(a). Sintering profiles have also been predicted for pellets exposed to different temperatures at a heating rate of 30 K/minute (30 °C/minute), and are compared with those obtained experimentally. Although all of them have similar profiles, for the sake of clarity, a few of them at low, intermediate and higher temperatures are shown in Figure 13(b).

Figure 13 depicts the sintering state of a pellet under variable heating rates that it experiences during a complete induration cycle. The predicted sintering states for the pellets exposed to different heating rates are in very good agreement with the experimental ones, whereas those exposed to different temperatures were found to deviate somewhat at lower temperatures but at higher temperatures they appears to be in good agreement. This may be attributed to the aforementioned reasons for the fluctuations in Figure 10 at lower temperatures. This establishes that by using the sintering

Fig. 12—Activation energies and pre-exponential factors for the sintering of magnetite pellets.

kinetic parameters, namely, n , K' , and Q , it can be possible to predict the extent of sintering for any non-isothermal profile using Eq. [9].

IV. DISCUSSION

The kinetic parameters of sintering, namely, time exponent, n , and the activation energy, Q , can be correlated to various sintering mechanisms. In the present study, the time exponent for magnetite sintering is found to be decreasing with increasing temperature, and two activation energies were deduced over the entire temperature range of study; suggesting two distinct mechanisms. Numerous investigations on solid state sintering^[15,35–44] have proposed n increasing with increase in temperature, and attributed the variation of n to various sintering mechanisms—surface diffusion ($n = 1/7$), grain boundary diffusion ($n = 1/6$), volume diffusion ($n = 1/5$), and viscous flow ($n = 1/2$). However, the current observations are not in correspondence with these propositions. Interestingly, the decreasing trend of n with increasing temperature for magnetite

Fig. 13—Predicted and estimated sintering ratios for pellets exposed to (a) different heating rates up to 1573 K (1300 °C), and (b) different temperatures at same heating rate of 30 K/min (30 °C/min).

sintering was also observed by Wynnyckyj and Fahidy.^[28] As far as activation energy is concerned, Xuebin *et al.*^[44] also found two activation energies for the sintering of hydroxyapatite over the temperature ranges, and are consistent with the current observations. In this context, further insights in to the current observations are being sought.

Magnetite is a non-stoichiometric ionic solid as shown in the FeO-Fe₂O₃ binary phase diagram in Figure 14 and has significant excess oxygen ions at higher temperature leading to defects which aid diffusion in these solids. It should be noted that for a fixed partial pressure of oxygen, the amount of oxygen dissolved in magnetite decreases with increase in temperature. Sintering mechanisms are primary diffusion based. Thus, a closer look at the diffusion in magnetite may throw some light in to their sintering kinetics estimated in the present study.

Many researchers have studied the cation tracer diffusion and jump frequency (Mossbauer spectroscopy) of magnetite in solid state^[45–56] with partial pressure of oxygen (p_{O_2}) and temperature. They found that diffusion of iron in magnetite lattice occurs by two different mechanisms—interstitial mechanism (at lower p_{O_2} and higher temperature) and vacancy mechanism (at higher p_{O_2} and lower temperature). It is also interesting to note that the activation energy for interstitial mechanism is positive whereas that for vacancy mechanism is negative. Thus, for a given p_{O_2} as temperature increases, the diffusion mechanism shifts from the vacancy to the interstitial mechanism. Such shift in mechanisms suggests that the activation energy increases when temperature increases from lower to higher, which does not imply with the current findings. Furthermore, for $p_{O_2} > 10^{-6}$ and temperature < 1573 K (1300 °C), vacancy mechanism is predominant which is plausible to operate in the range of temperatures being studied in the current investigation. However, the negative activation energy corresponding to this mechanism has also not been observed.

Fig. 14—The phase diagram for the system FeO-Fe₂O₃ showing the positions of the oxygen (atm) isobars.

Interestingly, Xuebin *et al.*,^[44] observed a trend in activation energy for the sintering kinetics of hydroxyapatite similar to that estimated in the current study for magnetite pellets. They correlated the kinetic parameters, n and Q to the morphology, which infers about the probable mechanisms responsible for sintering. They speculate that the high activation energy at lower temperatures is because of the initial neck formation through reaction and surface diffusion. Contemplating in the similar context for the findings of sintering of magnetite pellet, it might be a possibility that the bentonite/gangue minerals initiate neck formation through reaction and solid state diffusion at the initial

stages. Later at higher temperatures, there might be formation of liquid phase bridges^[57] decreasing the activation energy for sintering. Morphological studies using the automated image analysis of the microstructures of pellets can impart more insights into the sintering mechanisms at different temperatures. These studies are in progress and will be presented in future communication.

V. CONCLUSIONS

The sintering kinetics of magnetite pellet under inert atmosphere has been successfully estimated, in succession to oxidized magnetite pellet (hematite). Optical dilatometer is used to capture the shrinkage, and hence sintering of the pellet. Sintering is quantified using isothermal shrinkage data by estimating three kinetic parameters, namely, activation energy (Q) and pre-exponential factor (K') and a time exponent (n). The sintering of magnetite pellet shows that the value of ' n ' varies from 0.45 to 0.15 with the increase in temperature. The two activation energy values estimated for the sintering of magnetite pellets are 477 and 148 kJ/mole, respectively, at lower temperatures [1173 K to 1373 K (900 °C to 1100 °C)] and higher temperatures [1373 K to 1623 K (1100 °C to 1350 °C)] suggesting the possibility of two distinct mechanisms. The extent of sintering has been predicted under non-isothermal conditions as well by incorporating the variations in above mentioned kinetic parameters (n , K' , and Q) with temperatures, and are validated using experimental data.

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NOMENCLATURE

$\delta_{A,overall}$	Overall percentage area change at any instant during induration
$\delta_{A,sintering}$	Percentage area change due to sintering at any instant during induration
δ_A	Percentage area change at any instant
$\delta_{A,true}$	Percentage area change when pellet has no pores
α	Volumetric thermal coefficient of expansion
β	Area thermal coefficient of expansion
V_0	Initial volume of a material
V	Volume of material at any temperature

V_{true}	Volume of the pellet if it would have undergone complete sintering with no pores
T_0	Initial temperature ($t = 0$)
T	Temperature at any instant
γ	Sintering Ratio of the pellet at any instant in the isothermal section
γ^*	Sintering ratio at the start of the isothermal section
ρ	Bulk density of the pellet at any instant
ρ_{true}	True density of the pellet
ρ_0	Initial bulk density of pellet
t	Time for sintering reaction
t^*	Time corresponds if the pellet had attained a sintering ratio of γ^* from the start under isothermal condition
t_m	Measured time in isothermal section
n	Time exponent
K'_1	Pre-exponential factor at high temperatures
K'_2	Pre-exponential factor at low temperatures
Q_1	Activation energy at high temperatures
Q_2	Activation energy at low temperatures
R	Universal gas constant
γ_t	Sintering ratio at time t
$\gamma_{t+\Delta t}$	Sintering ratio at time $t + \Delta t$
Tt	Temperature at time t
$T_{t+\Delta t}$	Temperature at time $t + \Delta t$
$K(T_{t+\Delta t})$	Rate constant at $t + \Delta t$

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