

SINTERING MECHANISM OF MAGNETITE PELLETS DURING INDURATION

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Abstract

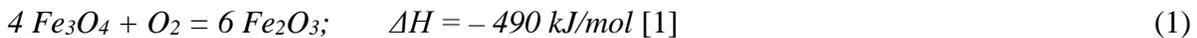
In Europe, Sweden has the richest magnetite ore deposits. The mined magnetite ore is ground, beneficiated and pelletized to make the process sustainable and environment friendly. These pellets are subsequently processed in blast furnaces, and hence the optimum pellet quality is of utmost important. Magnetite green pellets are indurated (heat hardened) in either rotary kiln or straight grate induration furnace to attain the quality standards in terms of strength and other metallurgical properties. The quality of magnetite pellet is primarily determined by the physico-chemical changes the pellet undergoes as it makes excursion through the gaseous and thermal environment in the induration furnace. Among these physico-chemical processes, the oxidation of magnetite phase and the sintering of oxidized magnetite (hematite) and magnetite (non-oxidized) phases are vital. Rates of these processes not only depend on the thermal and gaseous environment the pellet gets exposed in the induration reactor but are also interdependent on each other. Therefore, a systematic study has been done to understand these processes in isolation to the extent possible and quantify them seeking the physics.

Optical Dilatometer was used in a novel way to design the experiments on single pellets, exposed to different thermal profiles, in order to quantify the sintering of oxidized magnetite and non-oxidized magnetite, independently. Power law (Kt^n) and Arrhenius ($\ln(TK^{(1/n)}) = \ln K' - \frac{Q}{RT}$) equations quantifies sintering behavior by estimating three isothermal kinetic parameters, namely – activation energy (Q), pre-exponential factor (K') and time exponent (n). The values of activation energy and time exponent derived suggests that sintering of oxidized magnetite (hematite) is a single dominant diffusion mechanism, whereas sintering of unoxidized magnetite might be a combination of two distinct mechanisms; one operating at lower temperatures and the other at higher temperatures. The isothermal sintering kinetic equation is also extended to predict the non-isothermal sintering, and validated with the laboratory experiments. This will be further useful in predicting the sintering state of pellets during induration in the plant scale operations.

Introduction

Sweden possess the richest iron ore deposits in Europe. The ore gets leaner and leaner because of its continuous excavation over the period of time, and hence necessitates the recycling and reutilization of the ore fines in order to limit the particulate emissions in accordance to the stringent environmental guidelines. The fines, mostly generated during mining of the ores, dust emissions from the furnaces and the steel plant solid wastes, must be beneficiated and agglomerated, so that they can be reutilized in the metallurgical furnaces for subsequent processing into molten iron and steel. Pelletization is one of the widely practiced agglomeration technique, and more suitably for magnetite ore fines due to the exothermic nature of magnetite oxidation making the process energy efficient.

Pelletization utilizes ultrafine sized ore particles ($<150 \mu\text{m}$), mixed with binder (bentonite) and moisture. The resultant green (moist) pellets are strengthened by heat hardening up to the temperature of 1573 K in the oxidizing atmosphere where gas flow upward and downward across the bed during induration. The product pellets have fairly homogenous chemistry, uniform shape and narrow size distribution improving the bed permeability in subsequent iron making furnace (blast furnace). The pellets can also be stored and transported over long distances as input ferrous burden to various iron and steel manufacturers in different parts of the world. Therefore, pellets should possess superior quality, meeting the standards necessary for effective and efficient blast furnace operation. Pellet quality is primarily measured in terms of strength and reducibility, is an outcome of the evolution of crystal structure and morphology of the pellet. Magnetite pellet undergoes primarily two phenomena – oxidation and sintering during induration, and their extent depends on the heat transfer kinetics in the pellet exposed to the thermal excursion [1], [2]. The oxidation of magnetite is highly exothermic associated with the release of energy (Equation (1)) which raises the temperature within the pellet. The oxidation front propagates concentrically inward from the surface of magnetite pellet towards the center, forming a layer of hematite by the diffusion of gas through the pores. As the temperature inside the pellet increases, the pellet begins to sinter imparting adequate strength to it.



Ideally, it is desirable to have complete oxidation of the magnetite pellet followed by sintering but in industrial reactors, these phenomena might often proceed simultaneously. Since, the sintering of magnetite starts at lower temperatures than hematite sintering, the non-oxidized or unreacted magnetite in the core shrinks away from the hematite shell, thus forming a so-called duplex structure [1], [3], [4]. The duplex structure with non-oxidized magnetite core and oxidized shell often introduces structural stresses which might affect pellet quality, and hampers the effective blast furnace operation. This is further complicated by the heat generated within the pellet from the exothermic oxidation of magnetite, causing sintering of magnetite to occur earlier than otherwise. Therefore, it becomes necessary to understand and estimate the extent of each of the above mentioned phenomena. 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. The detailed findings of the study has been discussed elsewhere [5]-[7]. Further, such a model at the pellet scale can be integrated with models at the reactor scale to predict pellet quality for the given raw material mix exposed to a certain thermal profile.

Sintering is one of the critical phenomena during the induration process, especially, for magnetite pellets where it often occurs for both the phases – oxidized magnetite (hematite) and non-oxidized magnetite (magnetite) [1]. Sintering is a complex process involving transport of species by diffusion through various paths, such as bulk diffusion, surface diffusion, transport through the gaseous phases, etc., driven primarily to reduce the total surface energy [8]. Most of the sintering studies have been done on non-ferrous metallic powders and ceramics with the objective of achieving complete densification [9], [10]. On the other hand, sintering in iron ores is intended to impart enough strength and porosity into the pellet making them suitable to withstand the subsequent handling and operations in iron making furnaces. Thus, understanding the mechanisms of sintering kinetics at the initial stages are of interest for iron ores. This can be done by quantifying the sintering and deducing the kinetic parameters. Kinetics of process can be evaluated by estimating three kinetic parameters – time exponent (n), pre-exponential factor (K') and activation energy (Q) [11].

In 1974, Wynnyckyj and Fahidy [12] made an early attempt to study the sintering kinetics of pure hematite reagent powder and commercial magnetite concentrate in the form of briquettes under isothermal conditions. They proposed that the shrinkage of pellet during isothermal sintering can be used to quantify sintering, and correlated to the kinetic parameters by the Power law (Equation (2)) and Arrhenius law (Equation 3)) under isothermal conditions. Interestingly, there had not been any further quantitative studies on either magnetite or hematite sintering. Therefore, the focus of current investigation is to understand and quantify the process of magnetite sintering on pellet scale for both the phases (oxidized magnetite and non-oxidized magnetite) in isolation for further insights.

$$\gamma = Kt^n \tag{2}$$

$$\ln(TK^{(1/n)}) = \ln K' - \frac{Q}{RT} \tag{3}$$

Optical Dilatometer is used in a novel way to measure in-situ shrinkage of pellet instead of traditionally used push-rod dilatometer. It works on the principle of capturing the two-dimensional (2D) shadow images of the pellet sample by a 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, and therefore does not interfere in the process [13]. Experiments have been performed on single pellet scale for both oxidized magnetite and non-oxidized magnetite exposed to various gaseous and thermal atmospheres. The isothermal segments of the results have been analyzed to estimate the kinetic parameters. Further, the sintering kinetic equation is also extended to predict the overall sintering behavior of the pellet in non-isothermal as well as isothermal segment, using an appropriate mathematical modeling approach and validated by experimentation.

Experimental Details

The primary raw material used was the magnetite pellet concentrate collected from LKAB's mine in Malmberget, Sweden. The concentrate was targeted to have fineness of 65 % passing through 45 μm screens. The concentrate having $\text{Fe}_3\text{O}_4 > 95\%$ with Al_2O_3 and $\text{SiO}_2 < 0.6\%$, and 7 %

moisture by weight was mixed, with 0.5 % dosage of bentonite as binder, in a laboratory mixer (Eirich R02). The resultant green mix was then fed onto the laboratory drum pelletizer for balling, producing nucleation seeds (3.5 to 5 mm diameter) initially, and then continuous addition of green mix lead to the green pellets of desired size fraction (9 to 10 mm diameter). The green pellets was screened and collected. The green pellets were dried in an oven at 378 K overnight. 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 Helium pycnometer (AccuPyc II 1340) and a tailor-made Light Table Imaging (LTI) method, respectively, without hampering the pellet surface [5], [7]. The mean porosity of the pellet was then obtained from their skeletal and envelope densities.

Oxidized magnetite (hematite) pellets were prepared by oxidizing the dried magnetite pellet to hematite by placing them in a chamber furnace following a thermal profile in order to attain the degree of oxidation more than 90 %. The optimum oxidation temperature and holding time was found them to be 750°C and 4 hours, respectively [5]. The pellets were then cooled naturally to room temperature, and then transferred for sintering studies. Sintering experiments have been carried out in an optical dilatometer which works on the principle of light optics [5], [6], a schematic of which is shown in Figure 1.

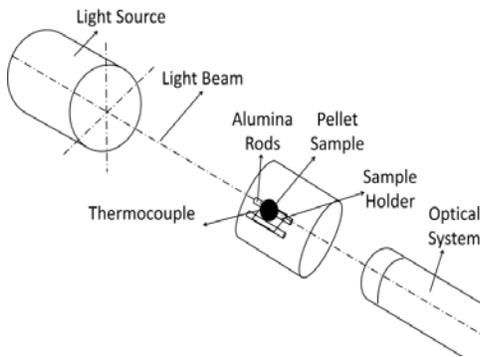


Figure 1: Schematic of Optical Dilatometer

Experiments were designed on the single pellet, independently, for oxidized and non-oxidized magnetite pellets. The thermal profile used for the studying the sintering is a combination of non-isothermal heating followed by the isothermal holding and the cooling section. This allows the thermal profile for the pellet more similar to the real situations. The holding time varies from 20 – 90 minutes for the desired sintering temperature so as the pellet have sufficient time for sintering. The experiments were executed at constant heating rate of 30 K/min to different peak sintering temperatures at intervals of 50 K for both the materials over the entire range of temperatures. The desired sintering temperature for oxidized magnetite chosen for the study ranges from 1423 – 1623 K and that for non-oxidized magnetite ranges from 1173 – 1623 K. The gaseous atmosphere maintained for sintering of oxidized magnetite was air (20% oxygen and 80% nitrogen) flowing continuously at an optimum flow rate of 0.3 liter per minute to avoid

deficiency of oxygen during induration, whereas inert atmosphere for sintering of non-oxidized magnetite by passing argon (99.995%) gas continuously at the maximum allowable flow rate of 0.5 liters per minute. This was done to keep positive pressure inside the furnace to avoid any oxygen infringement from the surroundings [7]. Further, for the purpose of validating the model developed for prediction of the sintering behavior of pellets, experiments are also designed at three different heating rates (15, 30, 45 K/min) to the isothermal sintering temperatures. The shadow images of the pellet were captured at an interval of 15 seconds during the whole thermal profile.

Results and Discussion

Shrinkage and Degree of Sintering

The shrinkage of pellet during sintering measured by capturing shadow images from optical dilatometer is in terms of the change in area fraction. The typical plot of the percentage area change with respect to time obtained from the optical dilatometer following a desired thermal profile is shown in Figure 2. The results from the optical dilatometer were found to be consistent and reproducible.

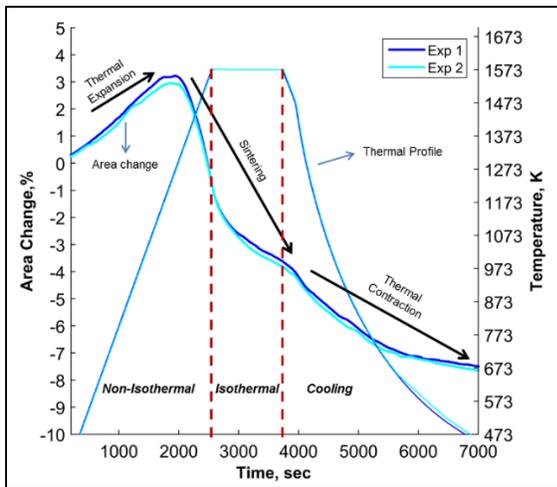


Figure 2: Typical plot for area change with time and temperature obtained from an optical dilatometer during induration of pellets

As mentioned above, the typical thermal profile for the induration of pellets consists of three segments – non-isothermal heating, isothermal holding, and furnace cooling. The pellet expands initially, and after reaching a maximum it begins to shrink under the influence of designed thermal profile. The expansion of the pellet initially is by the virtue of material property, and once the temperature reaches around 1173 – 1273 K, the sintering phenomena begins to dominate, resulting in the overall shrinkage of the pellet. Shrinkage in the isothermal regime is due to sintering alone and thereafter, during cooling, the pellet continues to shrink along with the influence of thermal contraction. Since, thermal expansion and thermal contraction are the

material properties, they were isolated from the overall change in area by comparing the slopes which provides the shrinkage of pellet due to sintering alone [5], [7]. As sintering is a thermally activated process, the degree of sintering for pellets increases with the increase in temperature as expected. It can also be noted that non-oxidized magnetite pellets sinter more than that of oxidized magnetite pellets when they are exposed to same sintering temperatures. This is because magnetite has begun to sinter from relatively lower temperatures as compared to hematite [1], [14].

Sintering Ratio

Sintering ratio (γ) for the pellets is defined as the ratio of the sintering accomplished to the sintering yet to be accomplished, and is used to measure and quantify sintering by capturing shrinkage. The sintering ratio rearranged in terms of area change due to sintering using the bulk density and true density is expressed as [5],

$$\gamma = \frac{\text{Sintering accomplished}}{\text{Sintering yet to be accomplished}} = \frac{V_0 - V}{V - V_{true}} = \frac{-\delta_{A,sintering}}{\delta_{A,true} + \delta_{A,sintering}} \quad (4)$$

where, $\delta_{A,sintering}$ is area change at any instant during sintering and $\delta_{A,true}$ is area change if the pellet would have been densely sintered.

Sintering Kinetic Parameters

Wynnyckyj and Fahidy [12] proposed that the isothermal sintering kinetics of iron ore pellets can be expressed by Power law (Equation (2)) and Arrhenius law (Equation (3)). This helps in determining the three essential kinetic parameters underlying the sintering mechanism. The variation in sintering ratio (as per Equation (4)) with time for one of the experiment is shown in Figure 3 illustrating the terms – sintering ratio and isothermal time.

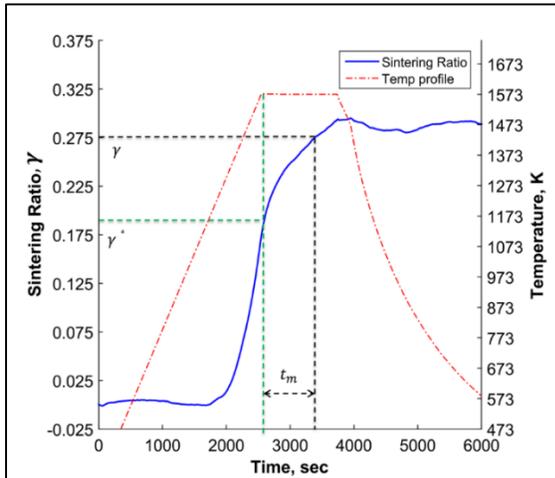


Figure 3: Parameters of power law from the plot of sintering ratio with respect to time

In order to estimate the sintering kinetic parameters, the isothermal segment of the curve is used. However, the time t of power law is the time starting from the instant if the pellet was kept under

isothermal condition from the start. But this was not the case for the experiments wherein the isothermal segments were always preceded by non-isothermal section. Therefore, an alternate methodology has been developed and derived an expression to estimate the kinetic parameters [5], [7].

$$\ln \left(\frac{\gamma}{\gamma^*} \right) = n \ln \frac{(t^* + t_m)}{t^*} \quad (5)$$

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 conditions.

The parameters n and t^* were estimated using least square fit for different experiments using Equation (5). The estimated parameters have been plotted for different sintering temperatures for oxidized and non-oxidized magnetite pellets, as shown in Figure 4. The linearity of the plots indicate that the power law is satisfactorily capturing the sintering kinetics for both types of pellets, even as the pellets were exposed to combined thermal profile, and their slope gives the value of 'n'. The value of time exponent 'n' for oxidized magnetite on an average was found to be 0.21 with standard deviation of 2.57 % over the entire range of temperatures (1423 – 1623 K), whereas the value of 'n' for non-oxidized magnetite decreases with increase in temperature, varying from 0.45 to 0.15 in the range of 1173 – 1623 K. A correlation between 'n' and isothermal sintering temperature (T) using a linear fit (with two data points considered as outliers) is expressed as Equation (6), which helps in predicting n as function of temperature.

$$n = -4 \times 10^{-4} T + 0.82 \quad (6)$$

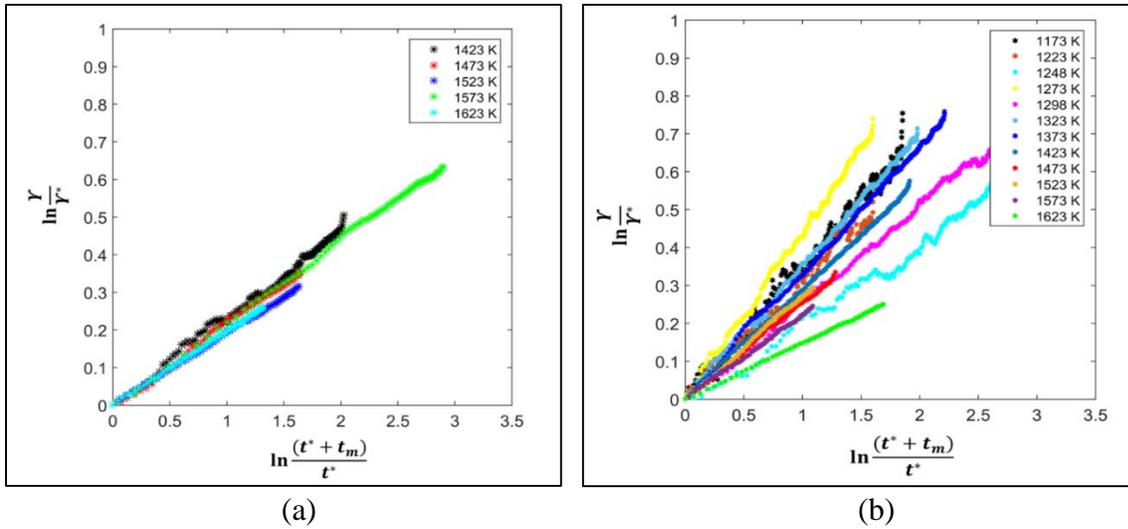


Figure 4: Plots of power law for (a) oxidized and (b) non-oxidized magnetite pellets

Further, the rate constant (K) is estimated for sintering temperatures and Arrhenius law (Equation (3)) is used to estimate pre-exponential factor (K') and the activation energy Q by plotting $1/T$ vs $\ln(TK^{(1/n)})$, as shown in Figure 6. The intercept and slope of plots following

Equation (3) deduce pre-exponential factor and the activation energy, respectively, for sintering of both oxidized magnetite and non-oxidized magnetite pellets. It can be inferred from the Figure 5 (a), that there is only one activation energy for sintering of oxidized magnetite pellets indicating that their kinetics is dominated by a single diffusion mechanism over the range of temperature [5]. On the other hand, sintering kinetics of non-oxidized magnetite pellets, as shown in Figure 5 (b), illustrate two separate slopes deducing two activation energies – one at lower (1173 K – 1373 K) and other at higher temperature ranges (1373 – 1623 K) suggesting the possibility of distinct sintering mechanisms [7]. This could be correlated to the morphology of the pellet, which infers the probable mechanisms responsible for sintering [15]. The most probable speculation for sintering of magnetite during induration is that the bentonite/gangue minerals initiate neck formation through reaction and solid-state diffusion at the initial stages contributing to high activation energy. Later, at higher temperatures, there might be formation of liquid phase bridges, decreasing the activation energy for sintering [14].

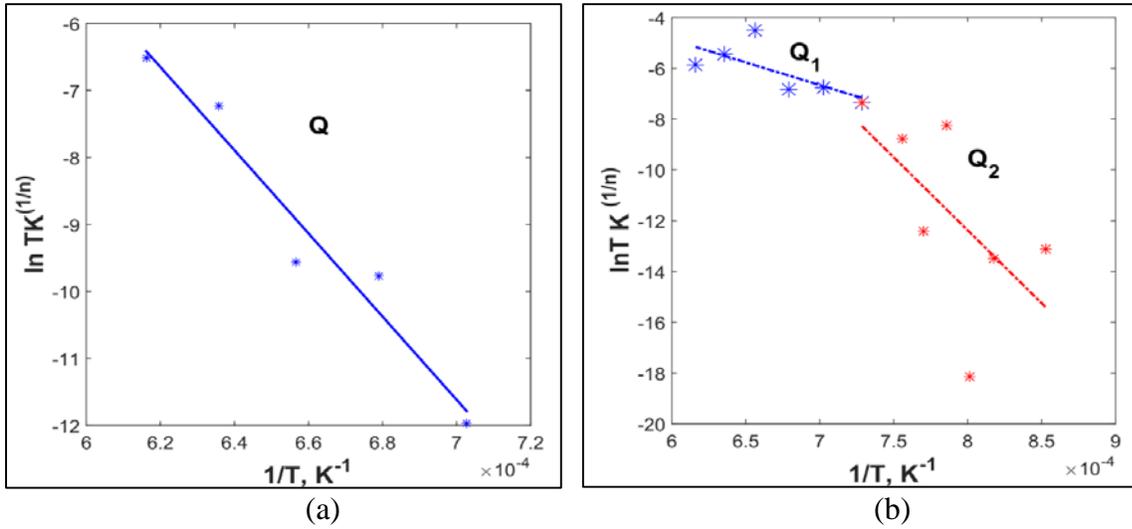


Figure 5: Estimation of Activation energy (Q) and pre-exponential factor (K') for the sintering of (a) oxidized and (b) non-oxidized magnetite pellets during induration

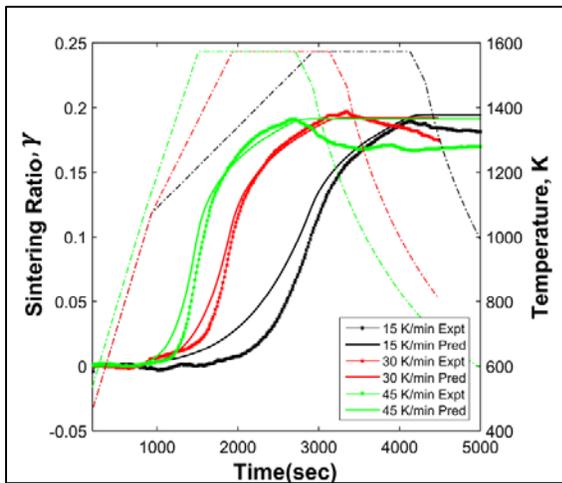
Prediction of Sintering profiles

In the industrial induration processes, sintering occurs under non-isothermal conditions. Variation of sintering ratio (γ) with time under isothermal conditions described by power law is extended to consider non-isothermal conditions. This new methodology is based on discretizing the entire time-temperature plot into small pseudo-isothermal steps and marching in time for a sufficiently small time step of Δt [5], [7]. The resulting expression for predicting the sintering ratio of pellets exposed to combined thermal profile is,

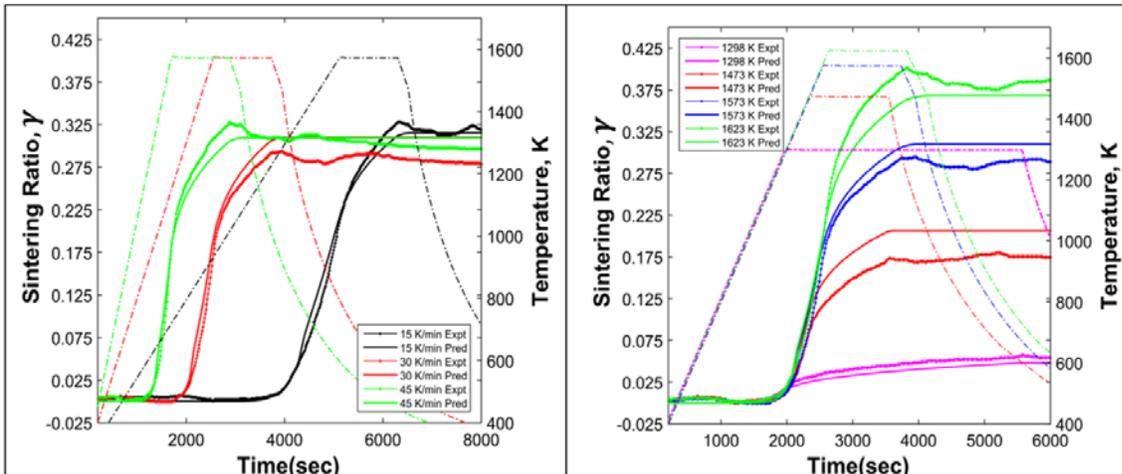
$$\gamma_{t+\Delta t} = K(T_{t+\Delta t}) \left(\left(\frac{\gamma_t}{K T_{t+\Delta t}} \right)^{1/n} + \Delta t \right)^n \quad (7)$$

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 $T_{t+\Delta t}$, whereas, $\left(\frac{\gamma_t}{K(T_{t+\Delta t})}\right)^{1/n}$ is the time that it would have taken to achieve sintering ratio of γ_t isothermally at temperature, $T_{t+\Delta t}$.

The predicted sintering ratio profiles for oxidized magnetite and non-oxidized magnetite pellets during sintering according to Equation (7) are compared with those obtained from the experiments at different heating rates (15, 30 and 45 K/min) and different isothermal sintering temperature, and are shown in Figure 6. The predicted sintering state (or sintering ratio) for oxidized as well as non-oxidized magnetite pellets were in quite good agreement with the experimental ones. Further insight onto correlating the morphological analysis with the experimental ones will throw more light to the understanding.



(a)



(b)

Figure 6: Prediction of sintering ratio for (a) oxidized and (b) non-oxidized magnetite pellets

Conclusions

The sintering kinetics of magnetite pellets on single scale during induration has been successfully estimated with the approach of capturing in-situ shrinkage, and quantifying them. Optical dilatometer is successfully used to capture the shrinkage, and hence sintering of the pellet, instead of traditionally used push-rod dilatometer. Sintering phenomena during induration of magnetite pellets are categorized into that of oxidized magnetite and non-oxidized magnetite, and studied independently. Sintering is quantified using isothermal shrinkage data by estimating three kinetic parameters – activation energy (Q), pre-exponential factor (K') and time exponent (n). The sintering of oxidized magnetite pellets happens by a single dominant mechanism, whereas, sintering of non-oxidized magnetite pellets happens possibly by two distinct mechanisms over the entire temperature ranges during induration. The sintering ratio for the both the pellets have been predicted for thermal profiles consisting of non-isothermal followed by isothermal conditions, and are validated using experimental data.

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List of Symbols

$\delta_{A,overall}$	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
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
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	Pre exponential factor
Q	Activation energy over entire temperature range
Q_l	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 $t+\Delta t$
T_t	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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