

Effect of Heating Rates on the Sintering of Oxidized Magnetite Pellets during Induration

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Summary

Magnetite pellet induration is a combination of complex physicochemical phenomena – oxidation, sintering and the heat transfer associated with them. Depending on the pellet properties and the environment it encounters during the induration, the oxidation and sintering course may vary and the mechanisms will interact. To be able to predict their course and control it, the kinetics of these phenomena needs to be understood. One approach is to determine the kinetics of the phenomena in isolation. The present investigation is aimed to predict and studying the sintering behavior of oxidized magnetite (hematite) pellets exposed to different heating rates. Experiments have been carefully performed at three different heating rates to capture the sintering behavior during induration using an optical dilatometer, and also used for validation.

Key Words

Induration, Sintering, Magnetite pellet, Optical Dilatometer

Introduction

Pelletization is the leading agglomeration technique practiced in across the world, especially for magnetite ore fines like in Sweden. Pelletization of magnetite aids an added benefit in terms of energy generated from exothermic nature of magnetite oxidation. Swedish steel industries pioneered in operating their blast furnaces with cent percent pellets. This makes it necessary to understand the entire process of pelletization, where green pellets are strengthened through heat hardening process for subsequent use in iron making units such as blast furnace and direct reduced iron processes.

Induration is carried out in a straight grate furnace or in straight grate furnace followed by a rotary 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 (273 – 523 K), oxidation (573 – 1073 K) at lower temperatures and sintering (> 1273 K) at higher temperatures¹. As the reaction front moves from the surface towards the center of the pellet by the diffusion of hot gases through pores, the oxidation should preferably precede the sintering. In reality sintering and oxidation may proceed simultaneously. This might for example causes the formation of a duplex structure in the pellet, with a magnetite core and hematite shell because of magnetite sintering which starts at a lower and thus inducing structural stress¹⁻⁴. The formation of the duplex structure is one of the reasons why it is necessary to understand the kinetics of the mechanisms involved in these processes thoroughly.

The methodology adapted was to study these processes in isolation, beginning with that of sintering of oxidized magnetite (hematite) pellet.

To understand the kinetics, the process has to be quantified and can be estimated by three parameters namely – Activation Energy (Q), Rate Constant (K') and time exponent (n). The sintering kinetics of oxidized magnetite was studied by capturing the shrinkage of pellet during its sintering under isothermal conditions⁵. These kinetics parameters have been estimated and discussed elsewhere⁶. The shrinkage during sintering of single oxidized magnetite pellet is being captured by optical dilatometer, which measures the dimensional variations solely on their optical images without having any contact with the sample, and hence does not interfere in the process^{6,7}. The activation energy and rate constant estimated for the sintering of oxidized magnetite pellet were 500 kJ mol^{-1} and $3.8 \times 10^{13} \text{ sec}^{-1}$, respectively. In this paper, these parameters have been used to predict and study the effect of different heating rates on sintering of oxidized magnetite pellet by conducting experiments.

Experimental Method

The source of magnetite chosen here is pellet concentrate from Luossavaara-Kiirunavaara AB's (LKAB) mine in northern part of Sweden. The concentrate was collected carefully by coning and quartering, and contains $\text{Fe}_3\text{O}_4 > 95 \%$ with Al_2O_3 and $\text{SiO}_2 < 0.6 \%$ and 7% moisture by weight. The concentrate was mixed with 0.5 % dosage of bentonite as binder in a laboratory mixer (Eirich R02). This green mix was then fed to drum pelletizer

(micro-balling) of 0.8 m diameter to produce nucleation seeds of 3.5 – 5 mm and subsequently balled into green pellets¹. The green pellets of desired size fraction of 9 – 10 mm were collected by screening. The smaller size of the green pellets than the widely used industrial average size (10 – 12 mm) for feeding into iron making units was decided based on the sample size limitations in the optical dilatometer. The green pellets were dried in oven at 423 K overnight.

The dried magnetite pellet was then oxidized to hematite by placing them in a chamber furnace to a degree of more than 90 %. The optimum oxidation temperature and holding time was found them to be 1023 K and 4 hours, respectively⁶. The pellets were then cooled naturally to room temperature, and then transferred to optical dilatometer as shown in Figure 1 for sintering at different heating rates. The pellets in all experiments were exposed to a thermal profile of 50 K/min from room temperature to 1023 K, and then to the sintering temperature of 1573 K at three different heating rates, low (15 K/min), medium (30 K/min) and high (45 K/min), and hold at that temperature for 20 min. Thereafter, the pellet was furnace cooled. A constant air flow rate of 0.3 liters per minute has been maintained across the pellet in the furnace throughout the experiment, so as to have sufficient oxygen available inside the furnace at any stage of sintering. The shadow images were captured continuously at an interval of 15 seconds to observe the shrinkage during sintering.

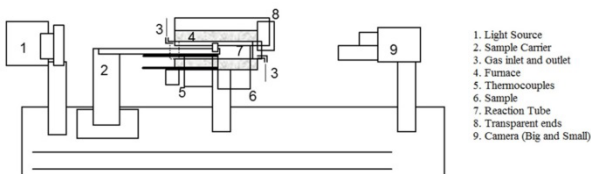


Figure 1: Schematic of Optical Dilatometer

The pellets were characterized for their moisture content, true density, bulk density and porosity at each stage i.e., dried, oxidized and sintered. Since the study is focused on single pellet experiments, it has been taken care that the surface of the pellet should not be contaminated while performing density measurements before and after each stage of the induration process, i.e., dried, oxidized and sintered on the same pellet. This has been achieved by using helium gas based Accupyc II 1340 for measuring true density of the pellet as whole with 10 cm³ cell volume, and tailor made Light Table Imaging (LTI) method for bulk density based on the principle of image analysis⁶. The mean porosity of the pellet can be obtained from their bulk and true densities.

Results and Discussion

The typical profile of percentage area change during sintering obtained from optical dilatometer is shown in Figure 2, for a given thermal profile. It has been assumed for these experiments that the temperature of the pellet at any instant of time is uniform within the whole pellet, which has been substantiated by laboratory experiments and analytical heat transfer calculations⁸.

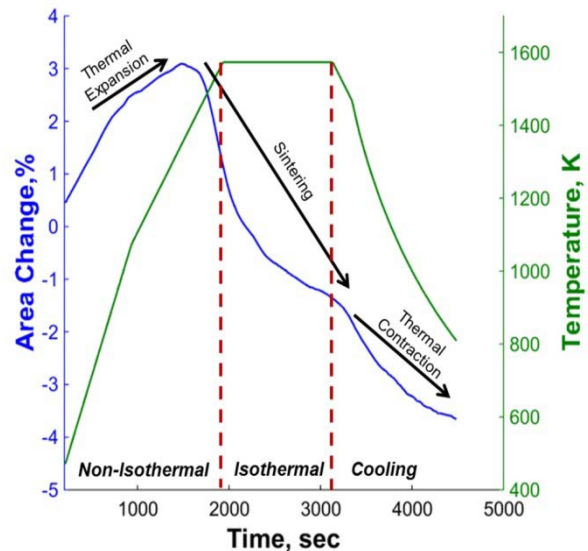


Figure 2: Typical Shrinkage curve obtained from Optical Dilatometer

As every material expands when exposed to heat, the pellet also expands initially during induration, and after reaching a maximum it begins to shrink under the influence of the thermal profile. After around 1273 K, the sintering phenomenon dominates resulting in overall shrinkage of the pellet. Shrinkage in the isothermal segment is mainly due to sintering alone, and thereafter the pellet continues to shrink in the cooling cycle because of thermal contraction. Therefore, the overall change in size of the pellet signifies the combination of the thermal expansion/contraction and the sintering phenomena.

Sintering degree & rate

Sintering degree is the amount of sintering that the pellet has achieved during the induration process represented in terms of shrinkage of the pellet. It is therefore necessary, to isolate the thermal expansion/contraction phenomena from the overall percentage change in area to obtain the shrinkage due to sintering alone. The amount that the materials will expand and contract under the influence of heating and cooling depends on their thermal coefficients of expansion and contraction. It is therefore, the percentage change in area is plotted as

a function of furnace temperature in Figure 3. It shows that the pellet expands linearly at low temperatures where sintering is insignificant, and as the temperatures goes beyond 1273 K the pellet begins to shrink non-linearly. During cooling also, the pellet shrinks linearly once the temperature has reached a sufficiently low level where sintering can be considered as insignificant. The slopes of these linear variations both during heating and cooling are equal.

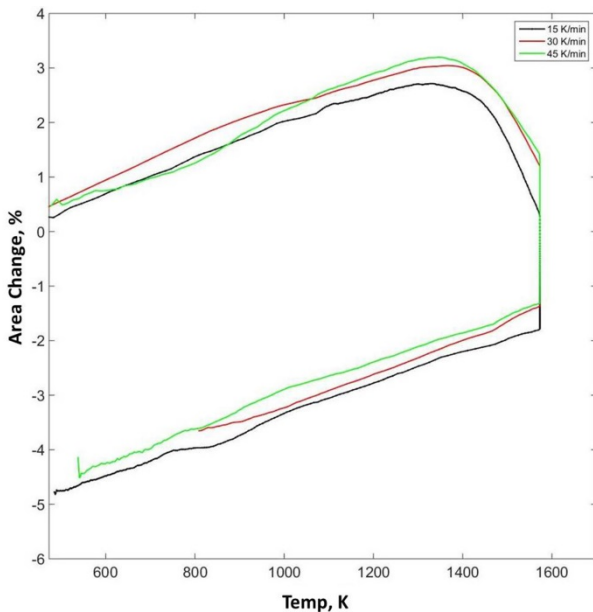


Figure 3: Change in area with respect to temperature of pellets for different sintering temperatures

It should be noted that the change in area of the pellet is measured from optical dilatometer and therefore the area thermal coefficient expansion (β) has to be related to volumetric thermal coefficient of expansion (α)⁸, and is expressed as

$$\beta = \frac{2}{3} \alpha \quad (1)$$

Since this is material property, the coefficient of thermal expansion estimated from Figure 3 would be equal to its contraction as well. It is therefore possible to isolate sintering alone from overall shrinkage of the pellet. It should be noted that the degree of sintering for the pellets exposed to different heating rates are similar as they have been sintered at same temperature (1573 K) as shown in Figure 3, but they have different sintering and decay rates as illustrated in Figure 4. Sintering rate is the rate at which sintering is progressing i.e., degree of sintering per unit time. Sintering rate of the pellet during the whole sintering time is shown in Figure 4. It can be observed that the pellet exposed to higher heating rate have higher rate of sintering in non-isothermal segment and also the higher rate of decay in the subsequent isothermal segment, and lower to that

exposed to lower heating rate. This is attributed to the fact that sintering is a thermally activated process whose rate of reaction front increases with increasing heating rates. Since, more number of the diffusion sites has been sintered during this segment at faster heating rate, there is less number of diffusion sites available for further sintering, and hence sintering rate decays at a faster rate.

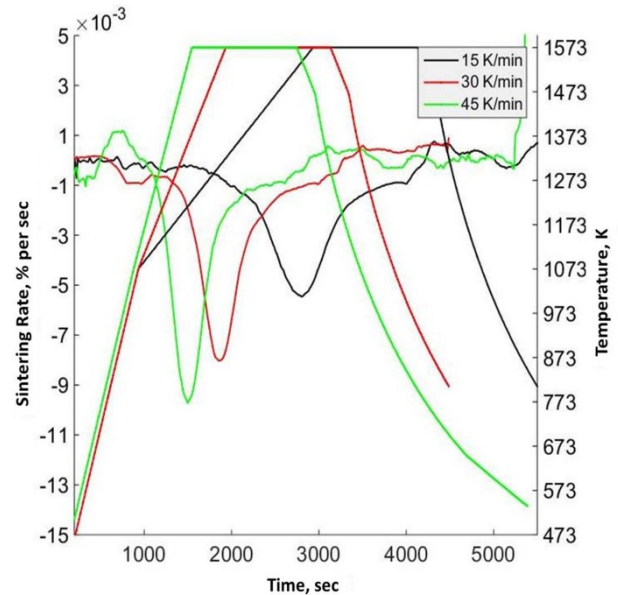


Figure 4: Sintering rate of with respect to time of pellets exposed to different heating rates

Sintering profile – prediction and validation

The sintering ratio (γ) can be used to evaluate the sintering profile which describes the state of the pellet during sintering. It is termed as the ratio of the sintering the pellet has accomplished to the sintering yet to be accomplished, also known as the extent of sintering⁴. It has been found that sintering ratio can help in estimating the sintering kinetics of material under a process by capturing its shrinkage.

$$\gamma = \frac{\text{Sintering accomplished}}{\text{Sintering yet to be accomplished}} = \frac{V_0 - V}{V - V_{true}} \quad (2)$$

where, V_0 is the initial volume of pellet, V is the volume of pellet at any instant during sintering and V_{true} is the volume if pellet would have undergone completely sintered with no pores remaining. Since the area change during sintering is obtained by isolating it from shrinkage, it can be related to bulk density of pellets measured by LTI and also to true density from Helium pycnometer. One can thus derive an expression for sintering ratio in terms of area change due to sintering as,

$$\gamma = \frac{-\delta_{A,sintering}}{\delta_{A,true} + \delta_{A,sintering}} \quad (3)$$

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. The sintering ratio obtained from equation (3) is then related to isothermal sintering time by power law (equation (4)) and Arrhenius law (equation (5)) to estimate the aforementioned kinetic parameters. The time exponent (n), activation energy (Q) and rate constant (K'), determined from studies on oxidized magnetite pellet exposed to different sintering temperatures (1373 – 1623K) at same heating rate (30 K/min) are 0.21, 500 kJ mol⁻¹ and 3.8 X 10¹³ sec⁻¹, respectively⁶.

$$\gamma = Kt^n \quad (4)$$

$$\ln(TK^{(1/n)}) = \ln K' - \frac{Q}{RT} \quad (5)$$

In the actual industrial induration process, sintering occurs under non-isothermal conditions. Variation of sintering ratio (γ) with time under isothermal condition described by equation (4) is extended to consider non-isothermal conditions by equation (6).

$$\gamma_{t+\Delta t} = K(T_{t+\Delta t}) \left(\left(\frac{\gamma_t}{K(T_{t+\Delta t})} + \Delta t \right)^n \right) \quad (6)$$

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 $T_{t+\Delta t}$. This has been derived by discretizing the time – temperature plot with small isothermal steps, such that at small time interval Δt sintering occurs isothermally at $T_{t+\Delta t}$ from γ_t to $\gamma_{t+\Delta t}$. $\left(\frac{\gamma_t}{K(T_{t+\Delta t})} \right)^{1/n}$ is the time that would have taken to achieve sintering ratio of γ_t isothermally at temperature $T_{t+\Delta t}$. The variation of γ can be obtained by knowing the temporal variation of temperature and the corresponding sintering rate constant, K , using equation (6) by marching in time for sufficiently small step of Δt .

The predicted sintering profiles are compared for validation with those obtained from the experiments conducted at different heating rates by equation (3) is shown in Figure 5. It depicts the sintering state of pellet under variable heating rates which it experiences during complete induration cycle comprising of non-isothermal heating followed by isothermal and thereafter cooling. The predicted sintering states for the pellets are in quite good agreement with the experimental ones. This demonstrates that with the use of sintering kinetic

parameters, namely, n , K' and Q , it is possible to predict the extent of sintering for any non-isothermal profile using equation (6).

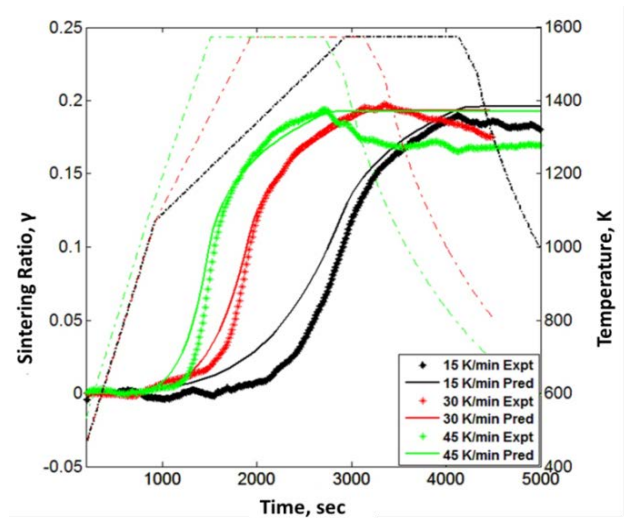


Figure 5: Predicted and Experimental Sintering Ratio (γ) for pellets exposed to different heating rates.

It can also be observed from Figure 5 that at any instant of sintering, the pellet exposed to higher heating rate has been progressed to higher extent of sintering, and that exposed to lower heating rate to lower extent. It also suggests that to attain a certain extent of sintering; pellet exposed to lower heating rates takes longer time as compared to that exposed to higher heating rates because of the slower rate of movement of sintering reaction front from the surface to the core of the pellet. It thus gives a handle to design the thermal profile for sintering of the pellet to optimize the sintering extent and time, and hence improving the operational efficiency and quality.

Conclusion

The effect of heating rate on sintering behavior of oxidized magnetite pellet in isolation has been successfully studied by capturing shrinkage of pellets in optical dilatometer. The pellet exposed to higher heating rates sintered at a faster rate and to a larger extent at any instant during sintering as compared to that exposed to lower heating rates. Quantitative description of sintering in iron ore pellets is useful in predicting the state of the pellet during industrial induration process. A methodology has been developed to predict the extent of sintering under non-isothermal condition using the three isothermal sintering kinetic parameters – Activation Energy (Q) and Rate Constant (K') and a time exponent (n). These predictions were validated using the experimental data, and found to be in good agreement with each other.

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References

1. Forsmo, S.P.E; Forsmo, S. E.; Samskog, P.O.; Björkman, B. M. T.: Mechanisms in Oxidation and Sintering of Magnetite Iron Ore Green Pellets; Powder Technology, vol. 183, No. 2, 2008, P. 247-259.
2. Semberg, P.; Rutqvist, A.; Andersson, C.; Björkman, B.: Interaction between iron oxides and olivine in magnetite based pellets during reduction at temperatures below 1000°C; Ironmaking and Steelmaking, 2011, 38, No. 5, P. 321-328.
3. Tang, M.; Cho, H.J.; Pistorius, P.C.: Early gaseous oxygen enrichment to enhance magnetite pellet oxidation; Metallurgical and Materials Transactions B, 2014, vol. 45 B, P. 1-11.
4. Wynnyckyj, J.R.; McCurdy, W.A.: Causes of the Shell and Core Structure and Layered Inhomogeneity in Iron Ore Pellets; Metallurgical Transactions, 1974, vol. 5, No. 10, P. 2207-2215.
5. Wynnyckyj, J.R.; Fahidy, T.Z.: Solid State Sintering in the Induration of Iron Ore Pellets; Metallurgical Transactions, 1974, vol. 5, No. 5, P. 991-1000.
6. Sandeep Kumar, T. K.; Viswanathan, N.N.; Ahmed, H.M.; Andersson, C.; Björkman, B.: Estimation of Sintering Kinetics of Oxidized Magnetite Pellet using Optical Dilatometer; Metallurgical and Materials Transactions B, 2014, vol. 45 B, P. 1-9.
7. Karamanov, A.; Dzhantov, B.; Paganelli, M.; Sighinolfi, D.: Glass Transition Temperature and Activation Energy of Sintering by Optical Dilatometry; Thermochemica Acta. 2013, vol. 553, No. 32, P.1-7.
8. Gaskell, D.R.: Introduction to the thermodynamics of materials; vol. 2, 5th ed., New York, USA: CRC Press, 2008.