Investigations on the Physico-Chemical Phenomena During Induration of a Magnetite Pellet

T. Kamesh Sandeep Kumar

Process Metallurgy
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Abstract

In the era of globalization with increasing environmental awareness, sustainable utilization of the available resources is a necessity; iron ores are no exception. Pelletization, being one of the increasingly practiced agglomeration techniques for the iron ore fines as well as other solid wastes from steel plants. The pellets produced are further fed into the metallurgical furnaces for subsequent processing. Induration is the vital cog in the process of pelletization, especially for magnetite ore fines. Induration of magnetite pellet is a complex physico-chemical phenomenon involving oxidation, sintering and the associated heat transfer.

Rates of these processes not only depend on the thermal and gaseous environment the pellet is exposed to in the induration reactor but are also interdependent on each other. A doctorate project was undertaken to systematically understand these processes in isolation to the extent possible and seek their physics by quantifying them with the overall objective of creating a single pellet model. Isothermal experiments on single pellet scale were designed to understand the sintering and oxidation behavior of magnetite pellets independently.

Sintering behavior of oxidized magnetite and non-oxidized magnetite pellets have been evaluated by continuously capturing their in-situ shrinkage using an Optical Dilatometer. The pellets were exposed to different thermal profiles in the defined range of temperature. The kinetics of sintering phenomenon was estimated with the help of power law and Arrhenius equations. The values of activation energy and time exponent derived suggests that sintering of oxidized magnetite (hematite) is dominated by a single diffusion mechanism, whereas sintering of magnetite showed two distinct mechanisms; one operating at lower temperatures and the other at higher temperatures. Further, in order to predict the sintering state of pellets during induration in plant scale operations, the isothermal sintering kinetic equation is also extended to predict the non-isothermal sintering. Thereafter, the predicted profiles were validated with the laboratory experiments, and found to be in fair agreement. Subsequently, these macroscopic sintering behaviors is correlated to quantitative microstructural characterization. This was done by quantifying the mosaic optical microstructures of pellet using the principle of distance transform.

Oxidation behavior of magnetite was studied by investigating the kinetics at both at particle and pellet scales. Isothermal experiments were designed with Thermo Gravimetric Analysis (TGA) at sufficiently low enough temperatures so that sintering effects are minimized. The experimental results were analyzed by Shrinking Core Model (SCM) and Avrami Kinetic Model (AKM). It was found from the fit that oxidation at particle scale suitably follows Avrami mechanism, which infers that the rate of oxidation is primarily determined by the rate of nucleation initially followed by the rate of growth. The activation energy of 226 kJ/mol suggests solid-state diffusion mechanism. These findings were corroborated by the microstructural evaluation of particles, where, the hematite crystals were seen growing in some preferred directions.

Further, the Pellet Oxidation Model is developed on the principles of grain model for gas-solid reactions by incorporating the derived particle oxidation kinetics with gaseous diffusion.
Interestingly, it was found from the experiments as well as from the model that there exist two peaks in oxidation rate curves for magnetite pellet oxidation. The intensity of the peaks increases with the temperature and shifts towards lower times. After investigating different cases, it was found that these peaks were attributed to the initial thermal transient as the pellet is lowered from room temperature into the isothermal zone of the reactor as well as initial high rates of oxidation at the particle scale. The earlier rise of peaks in the rate of oxidation curves for the pellets determined experimentally as compared to the model output could be because of the presence of large fraction of fine particles (size distribution) in the pellet instead of mono-sized particles. These findings were substantiated by microstructural investigations at pellet scale and particle scale. Thereafter, pellet oxidation model is used to predict the oxidation behavior of the pellets treated at higher oxidation temperature or enriching the oxygen content in the oxidizing gas. It is further intended to integrate the oxidation models and sintering models along with the associated heat transfer to develop the comprehensive Single Pellet Induration Model (SPIM). SPIM can be used as a tool to simulate the induration behavior of magnetite pellet at any stage during processing. In future, SPIM can be incorporated into the reactor scale models improving their efficiency, considering the raw material variability.
Acknowledgements

I express my sincere thanks and gratitude to my supervisor’s, Prof. Nurni N. Viswanathan for providing me the opportunity, continuous guidance and channelizing on technical front as well as many other areas of life; Dr. Charlotte Andersson for having critical inputs and discussions, helps in facilitating the best possible experimental and characterization resources, Dr. Hesham Ahmed for many crucial discussions as and when required, and efforts in managing things so that I can work smoothly, and Prof. Bo Björkman for valuable visionary inputs throughout the course of project. It has been wonderful working together as a group and hope to continue this animosity in future assignments as well.

I also thanks to Prof. Åke Sandström, who accepted to be my acting supervisor during my Licentiate exam in a short notice. I extend my greetings to Dr. Lawrence Hooey for his valuable feedback during Licentiate examination which helped me correct and improves the sintering models further.

Financial support from Hjalmar Lundbohm Research Centre (HLRC) is gratefully acknowledged.

I would also like to thank LKAB for providing the raw materials for the project and allowed to utilize their laboratory services for the experiments and characterization. I am thankful to many colleagues from LKAB for their support at various stages of my project, and to name a few; Ola Eriksson, Daniel Marjavaara, Anders Dahlin, Gustaf Magnusson, Axel Ståhlström, Klaus Weigel and Kjell-Ove Mickelsson. Thanks are due to Lars-Olof Nordin and Staffan Hedvall of LKAB Metlab, for sample preparation for the microstructural study, and Martin Simonsson (Data Ductus AB) for assisting in digitization of microstructure and further analysis.

I also thank Prof. N. B. Ballal, Prof. M. P. Gururajan (IITB) and Prof. S. Seetharaman (KTH) for valuable discussions in critical stages of the project.

I am greatly thankful to the colleagues and friends from Process Metallurgy, MiMeR and the Department of Civil, Environmental and Natural Resources Engineering (SBN) at LTU who have been around during my stay and LTU and made the Ph.D., a memorable and cherishable journey.

Finally, I would thank my family, especially my parents and my younger sister who continuously prays for my well-being and supported me throughout, even several miles away from home. I would take a moment and heartily thank an extremely special and lovable person, my life-companion Aparna Lohiya, who stood by me through all aspects of my life, personally, emotionally, sometimes technically as well, and truly a source of inspiration and motivation.

Thank You,
T. Kamesh Sandeep Kumar,
Luleå, 2018
List of papers

International Journals (peer reviewed)

Paper I
Estimation of Sintering Kinetics of Oxidized Magnetite Pellet Using Optical Dilatometer
- T. K. Sandeep Kumar, N. N. Viswanathan, H. Ahmed, C. Andersson and B. Björkman
(Metallurgical and Materials Transaction B, Volume 46B, Number 2, 2015, pp. 635 – 643)
(https://doi.org/10.1007/s11663-014-0273-y)

Paper II
Estimation of Sintering Kinetics of Magnetite Pellet using Optical Dilatometer
- T. K. Sandeep Kumar, N. N. Viswanathan, H. Ahmed, C. Andersson and B. Björkman
(Metallurgical and Materials Transaction B, Volume 47, Number 1, 2016, pp. 309 – 319)
(https://doi.org/10.1007/s11663-015-0505-9)

Paper III
Establishing a Novel Methodology to Correlate the Macroscopic and Microscopic Degree of Sintering in Magnetite Pellets during Induration
(Steel Research International, Volume 89, Number 3, 2018, pp. 1700366 (1-8))
(https://doi.org/10.1002/srin.201700366)

Paper IV
Investigating the Oxidation Kinetics of Magnetite on Particle Scale
(Accepted with minor revision to Metallurgical and Materials Transaction B, 2018)

Paper V
Developing the Oxidation Kinetic Model for Magnetite Pellets
(Submitted to Metallurgical and Materials Transaction B, 2018)
International Conferences contributions (not included in the thesis):

Studying the Sintering Behavior of Oxidized Magnetite Pellet during Induration
- T. K. Sandeep Kumar, N. N. Viswanathan, H. Ahmed, C. Andersson and B. Björkman
  (7th International Congress on the Science and Technology of Ironmaking (ICSTI): AISTech,
  May, 2015, Cleveland, United States of America)

Effect of Heating Rates on the Sintering of Oxidized Magnetite Pellets during Induration
- T. K. Sandeep Kumar, H. Ahmed, N. N. Viswanathan, C. Andersson and G. Magnusson
  (2nd European Steel Technology and Application Days (ESTAD): METEC,
  June, 2015, Dusseldorf, Germany)

Sintering Mechanism of Magnetite Pellets during Induration
- T. K. Sandeep Kumar, N. N. Viswanathan, H. Ahmed and C. Andersson
  (5th International Conference on Process Development in Iron and Steelmaking: SCANMET,
  June, 2016, Lulea, Sweden)

Investigating the Oxidation Phenomena of Magnetite Pellet
- T. K. Sandeep Kumar, H. Ahmed, C. Andersson, B. Björkman, A. Dahlin and N. N. Viswanathan
  (3rd European Steel Technology and Application Days (ESTAD): ASMET,
  June, 2017, Vienna, Austria)

Author’s contribution to the appended papers:

Most of the planning, experimental work, evaluation and writing were done by the author. Other co-authors have contributed in a supervisory capacity, timely discussions and reviewing the manuscripts.
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1 Introduction

In the current era of globalization, manufacturing industries play a vital role in the growth and development of a nation. Iron and Steel industries are particularly crucial, as steel finds its usage in virtually every application in the manufacturing, transportation, and construction; from surgical to automobiles, and therefore, per capita consumption of steel is considered one of the critical measures of development. Steel is the most sustainable and resource efficient material with maximum recyclability without loss of quality\(^1\). There is a continuous drive towards growth and progress, and hence, an increasing demand for steel. This in-turn increases the demand for hot metal (molten iron), which is met by the availability and supply of iron ores. Iron ore is mostly available on earth’s crust as hematite and magnetite. From the early 1900s, the iron ores of metallurgical grade has been reduced in smelting furnaces to molten iron and subsequently processed in oxidizing furnaces to steel.

Over time, the iron ore grades are getting leaner and leaner due to continuous excavation and with the increasing environmental awareness of particulate emissions to the atmosphere necessitated the need for recycling and reutilization of the iron ores. 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 recycled in the metallurgical furnaces for subsequent processing. Agglomeration is the size enlargement process whereby fine solid particles adhere to each other, and pelletization is one of the widely practiced agglomeration techniques\(^2\).

Unlike other agglomeration techniques, pelletization can utilize solid particles at ultra-fine scales; and going to finer scales enables liberation, which in turns helps in improved beneficiation. Pelletization uses much finer sized particles (<150 \(\mu\)m) as compared to that used in other agglomeration practices such as travelling grate sintering and briquetting (0.15 mm to 10 mm). It also has an edge in terms of physical and metallurgical properties, such as fairly homogenous chemistry, uniform shape and narrow size distribution. The pellets produced can also be stored and transported over long distances as the ferrous burden to various iron and steel manufacturers in different parts of the world.

Production of pellets from magnetite ore offers additional benefits in terms of being fuel efficient and environmentally friendly. This is because a significant part of heat for the induration process is produced through the exothermic oxidation of magnetite to hematite, according to Equation (1). The above-mentioned advantages of using magnetite pellets have led the Swedish steel industries in the 1980s to abandon the use of the other widely practiced agglomeration process – travelling grate sintering altogether, and pioneered in operating blast furnaces with cent percent pellets as the ferrous burden, and sometimes with minor proportions of briquettes.

\[ 4 \text{Fe}_3\text{O}_4 + \text{O}_2 = 6 \text{Fe}_2\text{O}_3; \quad \Delta H = -490 \text{ kJ/mol} \] \hspace{1cm} (1)
The pellets should possess superior quality, meeting the standards necessary for effective and efficient blast furnace operation. Pellet quality, primarily measured in terms of strength and reducibility, is an outcome of the additives and the induration the pellets undergoes. There have been many studies to understand the reactions taking place during pelletization of magnetite, i.e., physico-chemical transformations in the pellet. During induration, the magnetite pellet undergoes two important phenomena; namely, oxidation and sintering. The extent of these phenomena depends on the rate of reaction and heat transfer inside the pellet based on the thermal and gaseous composition. These phenomena during induration of magnetite pellet can be categorized in the Process Triangle, as depicted in Figure 1.

![Figure 1: Process Triangle for Induration of Magnetite Pellet](image)

Ideally, it is desirable to have complete oxidation of the magnetite pellet followed by sintering; although in industrial reactors, namely straight grate, rotary kiln and circular grate furnaces, often these phenomena might proceed simultaneously. Since magnetite sintering starts at lower temperatures than hematite sintering, the non-oxidized or unreacted magnetite in the core shrinks away from the hematite shell, thus introducing heterogeneity in the structure forming a so-called duplex structure. The duplex structure with non-oxidized magnetite core and oxidized shell often introduces structural stresses which might deteriorate the pellet quality. This is further complicated by the heat generated within the pellet from the exothermic oxidation of magnetite, causing sintering to occur earlier than otherwise. The extent of heterogeneity in the structure, its physical and chemical characteristics substantially alter the reducibility as well as the ability of pellets to descent through the ironmaking furnace without significant breakage. Therefore, it becomes necessary to estimate the rates and extent of these phenomena during induration, minimizing the amount of heterogeneity and predict the optimum thermal and gaseous profile for the given raw material mix.
Hence, modeling the pellet behavior during its excursion through the induration furnace could prove to be an effective tool. There are reactor scale models for predicting the overall performance of the induration furnace\textsuperscript{15-30}. However, their ability to predict the pellet quality is limited. In order to address these limitations, it is important that the physico-chemical phenomena during induration is quantitatively described at powder (particle) scale as well as at pellet scale, which can subsequently be integrated as input to the existing models at reactor scale.

A doctoral project at Lulea University of Technology (LTU) initiated for this purpose in collaboration with LKAB, is being financed by the Hjalmar Lundbohm Research Centre (HLRC). The overall goal is to create an appropriate mathematical model on pellet scale by systematically investigating the oxidation, sintering and the heat transfer phenomena, independently, to quantify the physics involved, and to understand the mutual interdependency of these phenomena, as mentioned in process triangle (Figure 1: Process Triangle for Induration of Magnetite Pellet).

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 by incipient fusion\textsuperscript{2,31-33}. It is one of the critical phenomena during induration process, especially, for magnetite pellets where it often occurs for both the phases – oxidized magnetite (hematite) and non-oxidized magnetite (Figure 1). It is, therefore, necessary to understand the process of magnetite sintering by quantifying and deducing the kinetic parameters.

Sintering kinetics have been studied since the early 1940s quite extensively in the field of powder metallurgy, whereas studies concerning the sintering kinetics of iron ore have been fewer in number\textsuperscript{31-33}. Wynnyckyj and Fahidy\textsuperscript{32} 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. Interestingly, there had not been any further quantitative studies on either magnetite or hematite sintering.

Oxidation is another critical phenomenon during induration of magnetite pellets. Unlike sintering studies, numerous studies on oxidation of magnetite pellets have been done, investigating the effect of different concentrate source, pellet and particle size distribution with respect to various thermal and gaseous atmospheres\textsuperscript{6,9,10,12,13,48-51}. Several gas-solid reaction models have been proposed to follow the reaction sequence for magnetite oxidation which provide the insight into the dominant mechanism in the range of variables studied\textsuperscript{5,6,52-56}. A large number of experimental studies to capture the oxidation behavior of magnetite on pellet scale have been performed, though very few were done on particle scale to understand their behavior\textsuperscript{6,9,12,13,48,49,57,58}. Since, pellet is comprised of several particles, the oxidation kinetics of particles is expected to affect the pellet oxidation.

Further, integration of such kinetic models for sintering and oxidation on the scale of the single pellet can provide the building blocks for reactor scale models. It will provide an aid to consider the variability in the raw material mix in future (backward integration) as well as predicts the optimum process control parameters to achieve the desired pellet quality (forward integration), which in turn helps to improve production efficiency.
2 Background

Iron ore mined and crushed into lumps of size 10 to 40 mm with Fe > 65 % is considered to be of the metallurgical grade for the efficient reduction in iron making furnaces. With the continuous excavation over the years, ores grades are getting leaner and leaner, both in terms of the availability of lumps and lower Fe content. The Fe content in these ores can be enhanced through the mineral beneficiation at fine scales. The ores beneficiated at fine scales calls for agglomeration techniques for their usage in iron making processes. Further, particulate emissions from the furnaces containing iron and carbon constituents affects the environment. This raises concerns over the environment, and government bodies have laid stringent constraints on the dust emissions from the plant as well as on carbon footprints\cite{59}. Therefore, to make the process more sustainable and environmentally friendly, there emerges the need to recycle and reutilize these fines. Agglomeration techniques play a crucial role in these efforts.

Agglomeration is the size enlargement process whereby fine particles adhere to each other, and heat hardened to form agglomerates which can be fed into the furnace as iron-bearing materials. Agglomerates intended for use in metallurgical furnaces should possess optimum quality parameters, as per the standards designed by the International Organization for Standardization (ISO) such as chemical composition (basicity), crushing strength (ISO 4700), tumbler and abrasive indices (ISO 3271), free swelling index (ISO 4698) reducibility (ISO 4695), reduction degradation under load (ISO 7992). There are three agglomeration techniques in practice; namely, briquetting, sintering (travelling grate) and pelletizing. Images of these products are shown in Figure 2.

![Figure 2: Iron ore agglomerates – a) Briquettes, b) Sinters, and c) Pellets](image_url)
2.1 Agglomeration Techniques

In briquetting, the fines in the size range of 0.15 mm to 3 mm are pressed against each other with the binder or without binders at certain pressures into blocks of suitable shape and size, and hardened\textsuperscript{2,60,61}. It is a matrix-distributed compaction process; therefore, the raw materials need to be thoroughly mixed to have the uniform distribution of binder, fluxes, and moisture. The green briquettes are further subjected to hardening either by hot briquetting or cold briquetting process depending on the desired compressive strength requirements.

Whereas, in travel grate sintering, the green mix of raw materials including coke breeze is laid as a packed bed onto the travelling strand with the permeable grate. The bed is then passed through an ignition hood, subjected to heating at high temperatures (1523 K (1250°C) – 1553 K (1280°C)) while moving continuously under the downdraft suction to produce the sinter cake\textsuperscript{2,61-65}. Sinter is the major iron-bearing burden which replaced lumps to about 60 – 85 % in blast furnaces. The limitation of travelling grate sintering process is that ultrafine particles (< 0.15 mm) cannot be used in the green mix, as this would affect the permeability of the bed, resulting in inferior quality sinters.

The limitations of travelling grate sintering and increasing environmental awareness necessitated the use of pelletization broadly in the early 1970s\textsuperscript{2,61,64-66}. Pelletization utilizes fines in the size range of microns as opposed to particles in millimeter size in briquetting and travel grate sintering. In pelletization, fine particles (< 150 μm or 0.15 mm) adhere to each other with the help of moisture and binding media, balled into spherical compacts and indurated to produce pellets with desired physical, chemical, and morphological properties.

2.1.1 Pelletization Process Flow

The pelletization process for magnetite ores can be broadly categorized into three sub-processes – raw material preparation, balling and induration, a schematic of the process flow is shown in Figure 3. Firstly, the magnetite ore is beneficiated and ground in ball mills by the wet grinding circuit. The output slurry of concentrate from ball mills having desired particle size distribution is sent to vacuum filters for the removal of excess moisture, producing the filter cake. In terms of size distribution, for good quality pelletization, 65 % of concentrate should be below 45 microns (Mesh #350)\textsuperscript{14}. The additives – fluxes and binder are added to the filter cake and mixed in a counter-rotating mixer while water is sprinkled to attain a homogenous green mix. The green mix containing 8 – 10 % moisture is rolled either in balling drums or discs to produce green pellets. After screening, the green pellets of desired size range (9 – 16 mm in diameter) are chosen for further processing, whereas under and over-sizes are recycled to the mixture. The green pellets are not strong enough to be used directly in the iron making furnace; therefore, they need to be strengthened by heat hardening process in an induration furnace.
Figure 3: Schematic of typical process flow sheet for magnetite pelletization

Figure 4: Typical thermal profile for pellet in different zones of Induration Furnace
During induration, the packed bed of green pellets undergoes drying, preheating, firing and cooling, as depicted in Figure 4. Updraft drying zone (UDD) mostly evaporates the moisture, followed by downdraft drying (DDD) at approximately 573 K (300°C) to gently release the chemically bonded hydroxides. After drying, the pellet bed reaches the preheating zone (PHZ) under downdraft suction and increases the temperature of the gas from 573 to 1553 – 1573 K (300 to 1280 – 1300°C), where a major part of the oxidation takes place followed by initiation of sintering. The oxidized pellets after preheating are exposed to firing zone (FZ), operating isothermally at 1553 – 1573 K (1280 – 1300°C), where particles inside the pellets get sintered (incipiently fused) in the solid state to each other by forming strong bonds. The firing of pellets can be done either in the straight grate, where the hot gases are sucked through the bottom of the bed or in the rotary kiln, where the pellets are exposed to a countercurrent flame of hot gas in the rotating drum. This is followed by final oxidation of the sintered pellets in the after firing zone (AFZ) at lower temperatures (~ 1273 K (1000°C)) and annular cooling zones (CZ1 and CZ2) to room temperature. The indurated magnetite pellets are collected and dispatched for further processing in iron making furnaces or shipped over long distances to various iron and steel manufacturers throughout the world.

2.2 Physico-Chemical phenomena during Induration

As depicted in Figure 1, oxidation, sintering and the associated heat transfer are responsible for the physico-chemical changes during induration of magnetite pellet. Wynnyckyj and McCurdy found that the extent of oxidation and sintering reactions during induration of magnetite pellets is responsible for the evolution of pellet morphology (microstructures). They found that the large shrinkage gradient in the pellet during induration leads to the formation of duplex structure (layered inhomogeneity), which is detrimental to the pellet quality. Papanastassiou and Bitsianes applied Unreacted Core Model (UCS) for oxidation of magnetite pellet and found that the oxygen potential and porosity are the major factors influencing the rate and progress of oxidation. Forsmo studied the influence of green pellet properties such as fineness of magnetite ore on the oxidation and sintering mechanism during pelletization. It was found that the finer the magnetite concentrate the faster is the rate of sintering for both the hematite and magnetite phases, leading to the formation of a larger fraction of unwanted duplex structure. Based on these observations, Cho et al. derived the oxidation kinetics and developed a suitable model to predict the size of the duplex structure. Tang et al. found oxygen enrichment enhances the degree of oxidation at lower temperatures before sintering begins, and hence, attempts to lower the fraction of duplex structure.

Additives also have a significant effect on the evolution of pellet quality. Bentell, Niiniskori and Friel et al. investigated dolomite fluxed magnetite pellets. They found that the presence of bentonite and low-melting dolomite flux adjacent to the magnetite particles promotes sintering by the formation of bridges preferentially along the grain boundaries, and imparts strength to the pellet. A similar observation was found by Firth and Garden in regards to the calcination of limestone and dolomite in magnetite pellets. Based on these findings, Firth attempted to model the calcination and oxidation reactions separately and collaborated to predict the extent of these mechanisms and
their effect on the microstructural evolution of the pellets. Granse\textsuperscript{69} found that vitreous slag formed is used to avoid the abnormal swelling in magnetite pellets during reduction. Recently, Semberg \textit{et al}.\textsuperscript{11} investigated different additives, such as quartz, limestone, dolomite, and olivine. They found that magnesium from the olivine flux diffuses farthest into the magnetite matrix at high temperatures under reducing atmospheres by forming magnesioferrite. This imparts sufficient high-temperature strength and improves reducibility in the blast furnace.

\subsection*{2.2.1 Sintering Mechanisms}

Sintering is a thermally activated phenomenon, where particles adhere to each other by diffusional mass transport of atoms, which has been studied for decades\textsuperscript{31,32,70-87}. The driving force for the sintering is the decrease in excess free surface energy of the irregularly shaped particles. The temperature of the sintering depends on the material and particle size. Mostly, the materials exhibit sintering temperatures equivalent to 0.5 – 0.8 times their melting temperatures. There are broadly three types of sintering, depending on the principal adhering phenomena – solid-state sintering, liquid-state sintering and pressure-assisted sintering.

The mechanisms during solid-state sintering of oxides can be determined from their path of mass transport depending on the driving force. They are classified into two categories – surface transport and bulk transport\textsuperscript{31,85}. The mass transport is mainly associated with the diffusion of atoms across different particle sites. The mode of dominant mechanism may vary depending on the temperature, particle size and extent of sintering. When the particles come close to each other, surface transport mechanisms (evaporation-condensation and surface diffusion), produce neck formation and grow without densification (shrinkage)\textsuperscript{31}. This is due to the mass flow originating and terminating at the particle surface. In bulk transport mechanisms (volume diffusion, grain boundary diffusion, plastic flow and viscous flow), the neck growth promotes densification (shrinkage) because the movement of mass is from the particle interior and deposited at the neck\textsuperscript{31}. Surface transport dominates at low temperatures, whereas bulk transport is mostly active at higher temperatures. Further, at even higher temperatures, the elementary stage of liquid sintering may sometimes become dominant and fastens rate of sintering. This could be due to the formation of low melting temperature slag, especially along the grain boundaries. The sinter bond between the particles in contact is the critical region because atoms are deposited there to reduce the surface energy. Generally, all the key sintering measures are related to the mass transport rates, subsequent neck growth, and pore changes\textsuperscript{31}.

\subsubsection*{2.2.1.1 Methods of evaluating Sintering Kinetics}

Kuczyński\textsuperscript{33} developed an early approach to estimate sintering kinetics while studying the sintering of alumina compacts by quantifying the microstructural observations; intermittently at predefined temperature intervals following the whole thermal profile. The extent of sintering was estimated from the microstructures of the alumina compacts at different temperatures with the help of a term
called neck size ratio. It is the ratio of neck size \( X \) to inter-particle distance \( D \) of the particle, which indicates the progress of sintering and is related to the green and sintered fractional density of the pellet, according to the Equation (2).

\[
\frac{X}{D} = 4 \left[ 1 - \left( \frac{\text{Green Fractional Density}}{\text{Sintered Fractional Density}} \right)^{1/3} \right]^{1/2}
\]

(2)

German developed the sinter model for very fine iron powder (20 μm) on the basis of neck size ratio as a measure for the extent of sintering, which helps to determine the diffusion mechanism dominant at any sintering temperature. It infers that at the low degree of sintering \( \left( \frac{X}{D} \approx 0.01 \right) \), particles attach together by adhesion at lower sintering temperatures, and as the temperature increases, neck size increases with the surface diffusion being the dominant mechanism. Whereas, at even higher temperatures, the dominant mechanism for mass transport is grain boundary diffusion agglomerating two particles by forming strong bonds, and finally, a fully dense \( \left( \frac{X}{D} \approx 1 \right) \) particle. The other transport mechanisms may still contribute to neck growth, even if they are not dominant. The effect of the simultaneous transport mechanisms is to increase the overall rate of neck growth, but possibly with a decreased rate of shrinkage. It was, therefore a time-consuming method and also prone to errors due to manual intervention.

Since sintering is accompanied by the shrinkage of the composite material, researchers have further utilized this feature as the basis to overcome the limitations of microstructural approaches and developed the methods to determine sintering kinetics by capturing the macroscopic changes. Dilatometers have been used to measure the dimensional changes of the compact because of shrinkage during the sintering process. Traditionally, a push–rod dilatometer based on the principle of Linear Variable Differential Transducer (LVDT) was used, where an alumina rod rests on the composite sample with a small amount of load (~5 to 20 grams) acting on it to sensitively capture the linear change in dimensions. It further assumes that the variation in dimensions is isotropic i.e., changes equally in all directions, during the sintering process, and hence estimate the change in relative volume and density of the composites. The ratio of relative change in these parameters during isothermal segment is related to the initial reaction mechanism by the power law and Arrhenius equation, to estimate the kinetic parameters – reaction rate and activation energy, as discussed in later sections.

Although this method is used extensively, there are a few limitations, which were reported by Karamanov et al. They studied the sintering kinetics of alumina composite by the recently developed optical dilatometer. It was found that the load exerting at the contact of push-rod with the sample might interfere with sintering kinetics of the material. The change in dimensions of the composite is anisotropic in reality, and assuming isotropic changes lowers the efficiency of the analysis. In addition, push-rod dilatometer is primarily designed for cylindrical composite, where the width to height ratio is 2:3. This allows the base of the alumina rod to rest properly on the
surface of the cylindrical sample, and thus, may not be appropriate for the spherical samples where only a single contact point exists at any random orientation. Therefore, an optical dilatometer based on the principle of light optics has been developed to capture the shrinkage of the pellet during sintering without any contact and hence does not interfere in the process kinetics. This might be advantageous in the near future and it may be used extensively for estimating the sintering kinetics for compacts of various materials.

2.2.2 Oxidation Mechanisms

Oxidation of magnetite pellet or particle is classified among the heterogeneous gas-solid reactions occurring in the metallurgical processes. Szekely et al.\textsuperscript{94} have carried out an extensive study to understand the gas-solid reaction system considering the structural parameters of solid particle/pellet system in the moving gas stream. During oxidation of magnetite, the reactant solid particle converted to the product solid when being exposed to oxidizing gas with the release of exothermic energy, as mentioned in Equation (1). The overall process involves following intermediate steps, which are rate controlling at different stages of reaction for the gas-solid reaction system, such as that for magnetite pellet oxidation:

- Mass transfer of reactant gas from the bulk to the internal surface of the reacting solid particle.
- Diffusion of gas through the pores of the solid or through the pores of the partially reacted solid.
- The intrinsic chemical reaction between the gas and solid at the gas-solid interface.

In addition, there are several other phenomena that may affect the progress of the reaction and the performance of the reactor in which the gas-solid reaction is carried out. These are heat transfer both within the reacting solid and between the solid and surrounding gas, structural changes because of the phase transformation, and the flow of gases and solids through the reactor. Several mathematical models have been developed to determine the kinetics of the dominant mechanisms and further predicts the conversion as a function of reaction time for solids. Doraiswamy and Sharma\textsuperscript{95} did an exhaustive review on the postulated models of gas-solid reactions, particularly for porous solids. Some of the models that are most relevant to the oxidation of magnetite pellet are briefly discussed here:

**Homogenous Model**

Homogenous Model (HM) is applicable to porous solids such that the reacting gas will penetrate through at rapid rate\textsuperscript{90}. This allows the reaction to proceed homogeneously throughout the porous solid. However, in some cases, diffusional gradients may exist in the pellet resulting in varying degrees of reaction within it. This approach is applicable to the highly porous bodies exposed at low
temperatures. The rate of reaction is then expressed as the product of available surface and surface reaction rate.

**Shrinking Core Model**
On the other hand, the Shrinking Core Model (SCM) is limited to a non-porous solid, where the reaction is assumed to occur at a sharp interface between the reacted outer shell and the unreacted core. Yagi and Kunii96 first proposed the SCM, and postulated that the reaction proceeds by the transfer of reactant gas through the gas-film or boundary layer surrounding the solid, diffusion of reactant gas inward through to the individual particles, chemical reaction at the gas-solid interface and then diffusion of product gas outward through the product layer and subsequently through the boundary layer. Therefore, as the reaction proceeds, the size of the unreacted core shrinks, and hence, the name of the model is shrinking core. It is also known as Sharp Interface Model (SIM) or Topo-chemical model.

**Finite Reaction Zone Model**
Finite Reaction Zone (FRZ) model assumes the reaction interface to be a diffused boundary of finite thickness and not a sharp boundary. A three-zone model postulated for general gas-solid reactions can further be reducible to simpler situations97. The reaction progress within a pellet can be categorized into three zones – exhausted zone, reaction zone and unreacted core. As the reaction progresses, the size of exhausted zone increases while that of unreacted core decreases. The finite reaction zone model reduces to SCM when the reaction zone approaches zero, whereas, it is analogous to homogenous model (HM) when the reaction zone is extended to the whole pellet.

**Grain Model**
Grain Model (GM), also known as Particle – Pellet model is most extensively used model for porous solids, where the reaction is assumed to happen over the diffused interface. This model postulates that the overall reaction of the porous pellet depends on the rate of diffusion of reactant gas via pores to reach the surface of non-porous particles, and the subsequent rate of conversion of individual particles98. As the reaction proceeds, the product layer formed on the periphery of particles will offer some resistance to the further diffusion of gases inside the pellet. This results in the varying extent of reactions at any instant of time across the different positions within the porous pellet. The mathematical approach of grain model is built by superimposing the rate of gas diffusion in the pores and the rate of reaction of the individual particles across the radial positions within the pellet.
2.2.2.1 Methods of evaluating Oxidation Kinetics

The exothermic oxidation of magnetite to hematite is accompanied by a weight gain, and the percentage weight gain is a measure of degree or fraction of oxidation. Therefore, in order to quantify the oxidation phenomenon, in-situ weight gain of the magnetite is captured continuously with respect to time in experiments and analyzed further to evaluate the kinetic parameters. The oxidation results are mathematically analyzed by adopting either of the aforementioned heterogeneous non-catalytic gas-solid reaction kinetic models. Oxidation proceeds from the periphery of the pellet further into the pellet through diffusion of oxygen. As the pellet, at the scale of 10 – 12 mm, consists of particles at the scale of 10 – 100 µm, locally at any location in the pellet, the oxidation occurs at particle scale. Therefore, the oxidation model needs to be developed both at particle and pellet scale. Among the various non-catalytic gas-solid reaction models, the Particle – Pellet or Grain model has been found to describe the oxidation phenomenon of magnetite pellets in the most appropriate manner. Most of the reported experimental studies have been performed at pellet scale, whereas, very few have investigated on particle scale to compliment the pellet oxidation.

Cho et al. investigated the magnetite oxidation, experimentally at particle and pellet scale. They adopted the concept of grain model for estimating the kinetics at pellet scale while assuming that the oxidation of individual particles proceeds by shrinking core mechanism with sharp reaction interface. They opine that the oxidation at the particle scale is determined by the intrinsic reaction kinetics as well as diffusion of oxidizing gas through the product layer. The diffusion can be through the product layer if there are any pores in the product layer, or it can be through solid state bulk diffusion, grain boundaries diffusion or diffusion through other imperfections in the product matrix. However, the activation energy reported from the studies using shrinking core model does not clearly point to any of these mechanisms in isolation.

On the other hand, Monsen et al. found that the needle-like structure of hematite grew ahead of the reaction front in magnetite particles instead of the sharp interface; suspecting that the reaction might not be fully described by SCM and there could be some other mechanisms contributing to it as well. Further, Monazam et al. examined the oxidation of secondary magnetite (i.e. reduced hematite) particles during Chemical Looping Combustion to understand the reaction mechanisms. They found that the oxidation kinetics at the particle scale is more appropriately followed by Avrami mechanism instead.

According to Avrami mechanism, the phase transformation often follows the sigmoidal (S-shaped) profile with initial slow rates owing to the formation of a sufficient number of nuclei (nucleation), thereafter increases at the rapid rate as nuclei grow into particles (growth) and cease slowly while approaching the complete transformation. They inferred that the particle oxidation proceeds by nucleation and growth, and growth of hematite into magnetite matrix is by solid state diffusion.
Thermo Gravimetric Analyzer (TGA) has been used extensively to estimate the isothermal oxidation kinetics to measuring the in-situ weight gain during the oxidation of magnetite particle as well as the pellet. Isothermal TGA studies can primarily be conducted in two ways: 1) By allowing the sample to reach the isothermal temperature in an inert gas atmosphere subsequently switching the gas from inert to the reactive one\textsuperscript{12,13,102} and 2) by inserting the sample in a short duration into the reactor zone kept at desired temperature and gas composition\textsuperscript{1}. Both these methods have associated disadvantages in terms of initial transients. In the former one, depending on the reactor volume and gas flow rates, it would take some time for the gas composition to reach a stable value. In the latter case, depending on the thermal capacity of the crucible and the sample, it would take some time before the crucible-sample assembly reached desired steady temperature.
3 Objective and Scope

The objective of the entire project is to develop a model that can simulate the induration behavior of a single magnetite pellet.

It will enhance the fundamental understanding of induration behavior of magnetite pellets, and can further be incorporated into reactor scale models to improve their efficiency. In order to begin from the basic, all the experimental work and thus also the modelling, has been based on a simplified pellet chemistry, not including other additions than the binder. This can be carried out by studying the induration process, comprised of sintering, oxidation, and heat transfer phenomena, in isolation to the extent possible. This can be done by quantifying these phenomena to deduce their kinetic parameters, and subsequently, integrating them together for simulating the overall induration behavior of magnetite pellets.

In the scope of this work, it is intended to quantify the sintering and oxidation phenomena independently with carefully designed experiments on the single pellet, deduce the kinetic parameters, develop and validate the mathematical model.
4 Methodology

During induration, sintering of magnetite pellets comprises of sintering of two phases – oxidized magnetite (hematite) and non-oxidized magnetite (magnetite). Therefore, to understand the overall sintering behavior of magnetite pellets, these two phases have further been investigated independently for quantification, and henceforth estimation of kinetics.

Optical dilatometer has been used for the first time in the current investigation to capture the macroscopic shrinkage of the single spherical pellet. Optical Dilatometer does not have any contact load or force on the sample as well as it captures the area shrinkage (two dimensional) during sintering, which adds an extra dimension to otherwise linear shrinkage (one dimensional). This helps in capturing the sintering process more efficiently.

Further, in order to capture the overall magnetite oxidation phenomenon during induration, TGA has been used to record the weight gain during oxidation for both, particles and pellets. Particles and pellets are introduced directly into the hot zone of the furnace. Small amounts of magnetite concentrate in the narrow size fraction is exposed to different temperatures and different partial pressures of oxygen in an oxidizing gas. This enables capturing the intrinsic reaction kinetics of the particles in the narrow size fractions, and minimize the influence because of particle size distribution of the concentrate. While shallow bed with small amounts of magnetite concentrate provides a uniform temperature throughout the experiment.

The macroscopic findings postulated during the current investigation have been supplemented by microstructural examination by using Light Optical Microscopy (LOM).
5 Experimental Plan

With the aim to capture the isothermal sintering of oxidized magnetite and non-oxidized magnetite pellets, experiments have been conducted on single pellet using optical dilatometer in the range of temperatures, as mentioned in Table I.

Table I: Experimental plan to investigate sintering of oxidized and non-oxidized magnetite pellets

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Sintering Temperature</th>
<th>Heating Rate</th>
<th>Isothermal Hold Time</th>
<th>Pellet</th>
<th>Sintering Temperature</th>
<th>Heating Rate</th>
<th>Isothermal Hold Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K (°C)</td>
<td>K/min (°C/min)</td>
<td>min</td>
<td></td>
<td>K (°C)</td>
<td>K/min (°C/min)</td>
<td>min</td>
</tr>
<tr>
<td>HP1</td>
<td>1423 (1150)</td>
<td>30</td>
<td>40</td>
<td>MP1</td>
<td>1173 (900)</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1223 (950)</td>
<td>30</td>
<td>MP3</td>
<td>1248 (975)</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>MP4</td>
<td>1273 (1000)</td>
<td>30</td>
<td>MP5</td>
<td>1298 (1025)</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>HP2</td>
<td>1473 (1200)</td>
<td>30</td>
<td>20</td>
<td>MP6</td>
<td>1323 (1080)</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>HP3</td>
<td>1523 (1250)</td>
<td>30</td>
<td>20</td>
<td>MP7</td>
<td>1373 (1100)</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>MP8</td>
<td>1423 (1150)</td>
<td>30</td>
<td>MP9</td>
<td>1473 (1200)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>HP4</td>
<td>1573 (1300)</td>
<td>30</td>
<td>20</td>
<td>MP10</td>
<td>1523 (1250)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>MP11</td>
<td>1573 (1300)</td>
<td>30</td>
<td>MP12</td>
<td>1623 (1350)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>HP5</td>
<td>1623 (1350)</td>
<td>30</td>
<td>20</td>
<td>MP13</td>
<td>1573 (1300)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>HP6</td>
<td>1573 (1300)</td>
<td>15</td>
<td>20</td>
<td>MP14</td>
<td>1573 (1300)</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td>HP7</td>
<td>1573 (1300)</td>
<td>45</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Further, isothermal oxidation experiments on particle scale considering three main parameters, namely, temperature, the partial pressure of oxygen and size fraction of the magnetite concentrate, as variables. These experiments are conducted in TGA, as mentioned in Table II, where the sample is introduced directly into the hot zone at the desired temperature.

| Table II: Experimental plan to investigate the oxidation of magnetite concentrate |
|----------------------------------|-----------------|-----------------|-----------------|
| Concentrate | Temperature, K (°C) | $p_{O_2}$ (atm) | Size Fraction, $d_p$ (μm) |
| P1 | 773 (500) | 0.21 | 38 to 53 |
| P2 | 823 (550) | 0.21 | 38 to 53 |
| P3 | 873 (600) | 0.21 | 38 to 53 |
| P4 | 923 (650) | 0.21 | 38 to 53 |
| P5 | 973 (700) | 0.21 | 38 to 53 |
| P6 | 1023 (750) | 0.21 | 38 to 53 |
| P7 | 1073 (800) | 0.21 | 38 to 53 |
| P8 | 873 (600) | 0.05 | 38 to 53 |
| P9 | 873 (600) | 0.10 | 38 to 53 |
| P10 | 873 (600) | 0.15 | 38 to 53 |
| P3 | 873 (600) | 0.21 | 38 to 53 |
| P11 | 873 (600) | 0.21 | 53 to 63 |
| P12 | 873 (600) | 0.21 | 63 to 74 |
| P13 | 873 (600) | 0.21 | 38 to 53 |
| P14 | 973 (700) | 0.21 | 38 to 53 |
| P15 | 1073 (800) | 0.21 | 38 to 53 |
| Non-isothermal |

Thereafter, oxidation behavior is also captured at pellet scale by experiments at constant temperature using TGA at three levels of temperatures and four levels of oxygen content in the oxidizing gas, as mentioned in Table III.

| Table III: Experimental plan to study the oxidation of magnetite pellets |
|----------------------------------|-----------------|-----------------|
| Experiment | Temperature, K (°C) | $p_{O_2}$ (atm) |
| Pellet 1 | 873 (600) | 0.21 |
| Pellet 2 | 973 (700) | 0.21 |
| Pellet 3 | 1073 (800) | 0.21 |
| Pellet 4 | 873 (600) | 0.15 |
| Pellet 5 | 873 (600) | 0.30 |
| Pellet 6 | 873 (600) | 1.00 |
6 Materials and Methods

6.1 Magnetite Concentrate

Magnetite ores from the mines of LKAB in Malmberget (Sweden) are ground, beneficiated and wet screened to produce the concentrate, which is used for pelletizing. In order to focus on investigating specifically the behavior of magnetite pellets; additives such as flux and other solid wastes have not been considered. The only additive used is bentonite which acts as a binder for the fine particles in the pellet. About 15 kg of concentrate has been collected at once, stored in containers and covered with paraffin sheets to avoid any absorption of extra moisture. This is to ensure that the raw material chemistry and properties remain constant for the experiments during the entire course of the project. The chemical and physical properties of magnetite concentrate (MPC) is mentioned in Table IV.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Physical Properties of Magnetite Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Magnetite Conc. (wt. %)</td>
</tr>
<tr>
<td>Fe</td>
<td>71.06</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.39</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.26</td>
</tr>
<tr>
<td>Σ Na₂O + K₂O</td>
<td>0.078</td>
</tr>
</tbody>
</table>

6.2 Preparation of Green Pellets

Green pellets are prepared from mixing the raw materials in a proportionate manner using balling drums, firstly by nuclei (seed) formation and subsequently their growth. The balling drum is 0.8 m in diameter, with the thickness of 0.15 m. Bentonite (0.7 wt. %) is added to concentrate and mixed in a laboratory mixer (Eirich R02, Germany) to form the green mix. Green mix (batch of 7 kg) is gradually scattered in the balling drum, rotating at 37 revolutions per minute (rpm) to prepare seeds (3.5 – 5 mm diameter). Moisture (0.5%) is added by spraying in short intervals over the scattered green mix until the optimum moisture requirement is achieved. The nuclei are fed into the balling drum, rotating at 47 rpm, and the green mix is added in parts over the nuclei to produce green pellets. The green pellets, thus produced are screened to achieve 75-80 % in the size range of
9 – 10 mm diameter. The green pellets are then dried at 378 K (105°C) for 8 hours, and stored in a desiccator to avoid moisture absorption.

6.3 Optical Dilatometer

Optical Dilatometer, which works on the principle of light optics has been used to capture the sintering phenomenon. A recently developed optical dilatometer by Misura HSM-ODHT, a schematic of which is shown in Figure 5 is used to continuously capture the in-situ shadow images of the sample exposed to the thermal profile. It measures the change in area (shrinkage) of shadow images (two-dimensional) with respect to temperature and time during the process.

![Figure 5: Schematic of Optical Dilatometer](image)

It comprises three principal units mounted on an optical bench: a continuously illuminated halogen light source, a horizontal tube furnace (100 mm in length and 20 mm in diameter) and an image capturing microscope with recording facility. It is equipped with a double-beam optical measuring system having two lenses attached to the image capturing device – one compatible for small samples (2 to 5 mm diameter), and the other for bigger samples (6 to 12 mm diameter). Therefore, the size of the pellet chosen is 9 – 10 mm, rather than industrially preferred 10 – 12.5 mm diameter. The pellet sample is placed on a small alumina plate (15 X 15 mm²) resting on a thermocouple inside the tube furnace, adjusted for focus, and the microscope transfers the image of spherical pellet sample from the furnace at 5x magnification through a quartz window and onto the recording camera. The typical thermal profile consist of non-isothermal heating, followed by holding isothermally at the desired temperature for a certain time duration and finally allowed the furnace to cool to room temperature. The entire set-up is assembled to a computer system facilitated with specific Misura
Thermal Analysis software to acquire and store the images of pellets subjected to a thermal profile at the predetermined time or temperature intervals.

Preliminary tests have been done to evaluate the difference between center and surface temperature of the pellet. It was found that it takes approximately 30 seconds to homogenize, well-complemented by analytical heat transfer calculations\(^{106}\). Therefore, it is reasonable to assume that the pellet has a uniform temperature throughout. Oxidized magnetite pellets are prepared by oxidizing the green pellet at 1023 K (750°C) for 4 hours in a chamber furnace, achieving more than 90% oxidation with no signs of sintering.

In case of oxidized magnetite, the air is flown continuously at the optimum rate of 0.3 liters per minute across the pellet in the furnace, in order to avoid stagnancy and probable deficiency of oxygen during sintering. Whereas, since magnetite is very prone to oxidation even at lower temperatures (around 673 K (400°C)), all the experiments are done under an inert atmosphere. This is done by passing argon gas continuously at the maximum allowable flow rate of 0.5 liters per minute, so as to keep the positive pressure inside the furnace to avoid any oxygen infringement from the surroundings. All the experiments have been repeated at least twice for reproducibility. The shadow images of the pellet in the process are preset to capture at an interval of 15 seconds for the whole thermal profile.

Further, experiments are also conducted, where pellets are exposed to varying heating rate for both oxidized magnetite and non-oxidized magnetite pellets. The thermal profile consists of non-isothermal heating at three different heating rates of 15, 30 and 45 K/min to the isothermal sintering temperature of 1573 K (1300°C), held for 20 minutes and cooled in the furnace.

6.4 Thermo Gravimetric Analyser (TGA)

Isothermal oxidation of magnetite particles and pellets is studied with the help of Thermo Gravimetric Analyzer (TGA) (Setaram 92). The TGA consists of a sample holder suspended from the weighing balance at the top and lowered into the graphite tube furnace with help of an elevator, as shown in Figure 6. While investigating the particle oxidation, about 27 mg of narrow size fraction particles \(d_p\) is poured in a platinum crucible (8 mm in diameter and 5 mm in depth) forming a shallow layer of approximately 3 mm. This is to maintain the resistance due to gas diffusion negligible and have homogenous temperature throughout. Whereas, the single magnetite pellet of 10 mm in diameter is suspended by placing it in a platinum wire basket.

Different proportions of O\(_2\) in N\(_2\) has been used as the oxidizing gas, mixed with the help of a digital gas mixer. The oxidizing gas is allowed to flow from bottom to top of the furnace at the rate of 200 and 300 ml/min for concentrate and pellet, respectively. These flow rates have been optimized by performing starvation tests. S-type thermocouple was placed beneath the hot zone to measure the temperature. The thermal excursion designed for each of the experiments comprises of heating the furnace up to the isothermal temperature at the rate of 20 K/min, held for 60 min followed by
cooling at the rate of 20 K/min under the desired oxidizing atmosphere. Once the gas atmosphere has been established and the isothermal temperature is reached, the sample is then lowered into the hot zone of graphite tube furnace (inner diameter = 15 mm and height = 300 mm) with the help of an elevator. Experiments are also conducted, where, the magnetite concentrate is oxidized non-isothermally from room temperature to desired isothermal temperatures at a heating rate of 20 K/min.

Background correction test has also been done for each experiment in TGA by using the empty platinum crucible by following respective thermal and gas profile. The in-situ weight gain is continuously captured at every one second by the data logger and corrected by background tests which are then used for further analysis.

6.5 Characterization

Characterization is an essential part of research to ensure that the experiments, analysis, and interpretation are aligned to derive appropriate findings. Characterization studies for the current work include density and porosity measurements, and Light Optical Microscopy (LOM).
6.5.1 Density and Porosity measurements

The two types of densities used for characterization of pellets are true density and bulk density. True or skeletal density is the ratio of mass to the volume of the sample excluding pores i.e., true volume. The true density of pellets is measured by means of a Helium Pycnometer (Accupyc II 1340, Micromeritics, USA). As experiments are designed on a single pellet, the same pellet is used for subsequent experimentation; therefore, the true density of the pellet needs to be measured in a non-destructive manner keeping the whole pellet intact. Hence, the sample cell of volume 100 cm$^3$ with an opening of 12 mm diameter is chosen for the same purpose. The true density of the pellet measured using helium pycnometer has a standard deviation of 1%.

On the other hand, measurement of bulk density without destroying the surface of the pellet is quite tricky. The bulk density or envelope density is measured usually by mercury porosimeter or fine sand powder pycnometer (Geopyc 1360 by M/s Micromeritics, USA), both of which hamper the surface of the pellet and hence cannot be used for further experimentation. This necessitates the development of a novel method of measuring bulk density in a non-destructive manner. This is achieved by using the setup of Light Table Imaging (LTI) developed by LKAB and MBV Systems AB. It captures the shadow images of the pellet placed on a brightly illuminated table with the help of a camera. The images are further analyzed by pixel count to determine the area fraction, and extrapolated to the volume of the pellet, assuming that the pellet is perfectly spherical, and divided by its weight to achieve the bulk density. A total of 20 images were taken for each pellet by orienting the pellet in different directions to capture the pellet surface from several angles to arrive at a statistically acceptable mean value. The correlating factor is found out to be 1.2, when compared with that determined by Geopyc, and is multiplied to the results of volume fraction obtained from analyzing the images from LTI.

Once bulk density and true density are measured, porosity can be determined by Equation (3).

\[
\text{Porosity, } \% = \frac{\text{True Density} - \text{Bulk Density}}{\text{True Density}} \times 100
\]  

Porosity evolved from the progress of the reaction inside the pellet is an indication of the sintering. The density and porosity values obtained for oxidized magnetite and dried magnetite pellets are given in Table V.

\[
\text{Porosity, } \% = \frac{\text{True Density} - \text{Bulk Density}}{\text{True Density}} \times 100
\]  

(3)
Table V: Density and Porosity values

<table>
<thead>
<tr>
<th></th>
<th>Oxidized Magnetite Pellets</th>
<th>Dried Magnetite Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>True Density (gm./cm³)</strong></td>
<td>5.30 – 5.45</td>
<td>5.15 – 5.40</td>
</tr>
<tr>
<td><strong>Bulk Density (gm./cm³)</strong></td>
<td>3.65 – 3.79</td>
<td>3.25 – 3.47</td>
</tr>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>27.72 – 30.34</td>
<td>32.39 – 36.98</td>
</tr>
</tbody>
</table>

6.5.2 Microstructural Evaluation

Light Optical Microscopy (LOM) by Zeiss (Imager.M2m) is used for studying the microstructures of the partially oxidized magnetite concentrate, oxidized and sintered pellets. The concentrate is sprinkled in the epoxy in subsequent layers, whereas, one half of the pellet sample cut by diamond saw is cold mounted in epoxy and are polished to a fineness of 1 μm with diamond pastes. LOM is integrated with image analyzing software provided by AxioVision. The microstructure of the whole pellet is generated, where the several images are progressively captured within a frame of 5 X 5 μm² at magnification of 200x across the pellet surface using the mosaic feature and are stitched together, as shown in Figure 7. The optical images of sintered and oxidized pellets exposed to different temperatures are captured at radial locations across the pellet cross section. Also, the optical images of partially oxidized single magnetite particle from the concentrate exposed to different oxidation temperatures are captured at the magnification of 1000x.

Figure 7: Optical microstructure of the pellet (shown in its entirety) generated by stitching several images together using the mosaic feature

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Further, an attempt to digitize the mosaic optical microstructures of sintered pellets has been done, where, the degree of sintering is estimated from the microstructures and correlated to the macroscopic findings. This has been done by applying the principle of distance transform, whereby, it measures the decrease in the perimeter of bonding particles associated with sintering. For this purpose, the optical images are corrected for illumination before stitching them together, classifies each of the pixels into different groups by applying the filters designed to enhance edges, extract texture and color/intensity information\textsuperscript{107,108}. Binary masks are created for each class and computed for the distance transform, as shown in Figure 8, resulting in the histogram of the distance map. Subsequently, sintering degree is estimated from the histogram, according to Equation (4)\textsuperscript{109}.

\[
\text{Sintering Degree} \% (\gamma) = \frac{\text{Cum. fraction of sintered particles in thermally treated pellet}}{\text{Cum. fraction of particles in green pellet}} \times 100
\]  

Figure 8: (a) Optical microstructure of a pellet at the gray level processed to create the (b) binary mask (one (1) = hematite or magnetite phase and zero (0) = pores) and (c) the distance transformed image (pixel layer-wise color on the perimeter)

### 6.5.3 Quench Tests

Magnetite green pellets dried at 423 K (105°C) are kept in the steel-wire basket, and inserted in the vertical tube furnace at an oxidation temperature of 973 K (700°C) and oxygen partial pressure of 0.21 atm at the flow rate of 300 ml/min. The partially oxidized magnetite pellets were taken out from the furnace after oxidizing for 120, 240 and 480 secs. The partially oxidized magnetite pellets were quenched instantaneously by inserting them into the nitrogen bath. Thereafter, the magnetite pellets oxidized have been examined microstructurally.
7 Results, Analysis and Discussion

7.1 Sintering

The results of the sintering experiments from the optical dilatometer for oxidized magnetite and non-oxidized magnetite pellets are further analyzed in this section to derive the kinetic parameters and develop the sintering model.

7.1.1 Sintering Ratio

Sintering ratio ($\gamma$) for the pellets is defined as the ratio of the sintering accomplished to the sintering yet to be accomplished, as shown in Equation (5), and is used to measure and quantify sintering by capturing shrinkage.

$$\gamma = \frac{\text{Sintering accomplished}}{\text{Sintering yet to be accomplished}} = \frac{V_0 - V}{V - V_{true}} \quad (5)$$

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 optical dilatometer measures the change in the area of pellet during sintering, 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 ($\gamma$) in terms of area change due to sintering ($\delta_A,sintering$), according to Equation (6).

$$\gamma = \frac{-\delta_A,sintering}{\delta_{A,\text{true}} + \delta_A,sintering} \quad (6)$$

where $\delta_{A,\text{true}}$ is the change in the area corresponding to completely sintered and dense pellet.

This sintering ratio exposed to thermal profile comprising of non-isothermal segment followed by isothermal is plotted with respect to time for oxidized magnetite and non-oxidized magnetite pellets, in Figure 9. It is observed that sintering ratio rises sharply at the initial stages and slowly thereafter, in correspondence to the rate of sintering. Higher rate at the beginning is attributed to the high pore volume initially, and decreases continuously with the increase in reaction extent. It is found that sintering ratio increases with temperature for both oxidized magnetite and non-oxidized magnetite pellets. Also, due to material properties, non-oxidized magnetite pellet achieves higher sintering
ratio as compared to that for oxidized magnetite pellet for the given temperature. The dip in the sintering ratio for sintered pellet at the end of the isothermal segment might be attributed to the change in thermal segment from the furnace controller. The isothermal sintering ratio is further used for determination of the kinetics.

Figure 9: Sintering ratio with time for (a) oxidized magnetite and (b) non-oxidized magnetite pellets exposed to different isothermal sintering temperatures during induration

7.1.2 Estimation of Sintering Kinetic Parameters

Since, the rate of sintering progressively decreases with time at a constant temperature; and as the driving force minimizes with the increasing extent of sintering; the variation of sintering ratio with time is not expected to be a linear relation. Therefore, Wynnyckyj and Fahidy\(^3\) proposed that the isothermal sintering kinetics of iron ore pellets is expressed by Power law (Equation (7)).

\[
\gamma = Kt^n
\]  
\(7\)

where \(t\) is the isothermal time, \(n\) is time exponent and \(K\) is rate constant.

Whereas, sintering is a thermally activated process, the rate constant, \(K\) is expected to follow Arrhenius law and is expressed as **Equation (8).**
\[
\ln(TK^{(1/n)}) = \ln K' - \frac{Q}{RT}
\]  

(8)

Here, \(Q\) is the activation energy at the isothermal temperature \(T\), \(K'\) is the pre-exponential factor, and \(R\) is gas constant.

This is used in determining the three essential kinetic parameters, \(n\), \(Q\) and \(K'\), underlying the sintering mechanism. The variation in sintering ratio with time is shown in Figure 9. In order to estimate the sintering kinetic parameters, the isothermal segment of the curve is used. However, as mentioned earlier, the time \(t\) of Equation (7) is the starting time if the pellet was kept under isothermal condition from the beginning. But this is not the case for experiments wherein the isothermal segments were always preceded by non-isothermal section due to some constraints in the equipment. Therefore, an alternate methodology was developed to obtain the kinetic parameters.

Let us denote, \(y^*\) as the sintering ratio at the start of the isothermal section. Thus, it is possible to define a time, \(t^*\), which corresponds to a time if the pellet had attained a sintering ratio of \(y^*\) from the start under isothermal conditions. If so, Equation (7) can be written as,

\[
y^* = K(t^*)^n
\]  

(9)

And beyond \(t^*\),

\[
y = K(t^* + t_m)^n
\]  

(10)

where \(t_m\) is the time measured from the start of the isothermal section.

From the Equations (10) and (11),

\[
\ln \left( \frac{y}{y^*} \right) = n \ln \left( \frac{t^* + t_m}{t^*} \right)
\]  

(11)

Using the data of sintering ratios from the isothermal segment and Equation (11), the parameters \(n\) and \(t^*\) are estimated using a least square fit for different experiments. Further, the isothermal sintering ratio is plotted with respect to time, according to Equation (11) for oxidized and non-oxidized magnetite pellets exposed to different temperatures, as shown in Figure 10. The straight lines indicate that the power law (Equation (7)) is satisfactorily capturing the sintering kinetics, even as the pellets are exposed to combined thermal (non-isothermal followed by isothermal) profile rather than only isothermal.
However, it can be observed that at lower temperatures, especially for non-oxidized magnetite pellets there are significant fluctuations in the straight line, whereas at higher temperatures the fluctuations are much less. This might correspond to the fact that at lower temperatures the variation in shape and packing of particles in the pellet, may be influencing the initial sintering phenomenon. 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.

The slope of the straight lines from Figure 10 provides the \( n \) value. It is interesting to note that the value of the time exponent \( n \) for oxidized magnetite is found to be in a very narrow range, whereas that of non-oxidized magnetite varies over a range of sintering temperatures. Therefore, it is appropriate to consider a mean value of \( n \) for oxidized magnetite which was found to be 0.21 with the standard deviation of 2.57%. The value of \( n \) for non-oxidized magnetite decreases with increase in temperature, as shown in Figure 11, from 0.45 to 0.15. A relation between \( n \) and the isothermal sintering temperature \( (T) \), using a linear fit (with two data points considered as outliers), is expressed as Equation (12), which used in predicting \( n \) as function of the temperature.

\[
n = -3.63 \times 10^{-4} T + 0.813
\] (12)
Further, Arrhenius law (Equation (8)) is used to estimate the pre-exponential factor ($K'$) and the activation energy ($Q$) by plotting $\frac{1}{T}$ vs $\ln(TK^{1/n})$, as shown in Figure 12. From the intercept and slope of plots, the pre-exponential factor and the activation energy, respectively, for sintering of both oxidized magnetite and non-oxidized magnetite pellets can be deduced. It can be inferred from the Figure 12(a), that the sintering of oxidized magnetite pellets is dominated by a single diffusion mechanism in the range of temperature studied, with the activation energy of 509 kJ/mol. Sintering of non-oxidized magnetite pellets, as shown in Figure 12(b), illustrate two separate slopes from which two activation energies - 477 kJ/mole (1173 K – 1373 K (900 – 1100°C)) and 148 kJ/mole (1373 – 1623 K (1100 – 1350°C)) is deduced. The activation energy deduced for sintering of non-oxidized magnetite pellets at lower temperatures is higher than at higher temperatures, suggesting distinct sintering mechanisms at lower and higher temperatures.
7.1.3 Sintering Prediction using Kinetic Parameters

In the industrial induration processes, sintering occurs under non-isothermal conditions. Variation of sintering ratio ($\gamma$) with time under isothermal conditions described by Equation (7) is extended to consider non-isothermal conditions using the following methodology.

Let $\gamma_t$ 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 $T_{t+\Delta t}$. During this time interval $\Delta t$, assume that sintering occurs isothermally at $T_{t+\Delta t}$ from $\gamma_t$ to $\gamma_{t+\Delta t}$. This is equivalent to discretizing the time-temperature plot with small isothermal steps. If so, the sintering during this time interval $\Delta t$ can be written as,

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

where, $\left( \frac{n}{k(T_{t+\Delta t})} \right)^{1/n}$ is the time that it would have taken to achieve sintering ratio of $\gamma_t$ isothermally at temperature, $T_{t+\Delta t}$.
The variation of $y$ can be obtained by knowing the temporal variation of temperature and the corresponding sintering rate constant, $K$, using Equation (13) by marching in time for a sufficiently small step of $\Delta t$.

Further, in order to validate the developed sintering model, the predicted sintering behavior for oxidized magnetite and non-oxidized magnetite pellets are compared with those obtained from the experiments at different heating rates and are shown in Figure 13. The predicted sintering behavior of pellets are in quite good agreement with those determined experimentally. This demonstrates that by using the sintering kinetic parameters; namely $-n$, $K'$ and $Q$, it is possible to predict the extent of sintering for any non-isothermal profile using Equation (13).

![Figure 13: Prediction of sintering ratio for (a) oxidized magnetite and (b) non-oxidized magnetite pellets exposed to isothermal sintering temperature of 1573 K (1300°C) at different heating rates (15, 30 and 45 K/min)](image)

7.1.4 Microstructural Evaluation of the Sintering degree

Optical microstructures of the entire pellet (mosaic optical microstructures) were acquired and inspected for all the sintered pellets considered in the study. For brevity and clarity, a thin strip of the microstructure from each of the mosaic optical images is presented in Figure 14.
Figure 14: Optical microstructures for oxidized magnetite (OM) and non-oxidized magnetite (M) pellets with respect to a green pellet over the temperature range 1423–1623 K.
For both oxidized and non-oxidized magnetite pellets, an increase was observed in the extent of sintering with temperature, with the green pellet as the reference sample. This result was expected and consistent with the theoretical understanding of the sintering phenomenon.\textsuperscript{33,66,110} This encourages further to estimate the sintering degree quantitatively by digitizing the mosaic optical microstructures of sintered pellets and correlate it with that determined macroscopically by optical dilatometer. The microscopic sintering degrees estimated for both the pellet groups in the range of temperatures studied are compared with those obtained from optical dilatometer, as shown in Figure 15.

![Figure 15](image)

Figure 15 : Comparison of sintering degrees from the optical microstructures (microscopic) and optical dilatometry (macroscopic) for (a) oxidized magnetite and (b) non-oxidized magnetite pellets

The profiles of sintering progression with respect to temperature are in fair agreement with each other for both oxidized and non-oxidized magnetite pellets. However, a slight scatter in sintering degree is observed in the values estimated by microstructural image quantification for non-oxidized magnetite pellets at lower temperatures (1173 – 1373 K (900 – 1100°C)); this scatter may be due to limitations imposed by the resolution of the smaller grains in the optical microstructures of the pellets exposed to low sintering temperatures.

This methodology of quantifying microstructural images to estimate sintering degree is a step towards understanding and capturing the sintering behavior more closely in a semi-automated manner. Once the methodology is further fine-tuned and validated over several types of pellets, the development of an online module in future can be planned to determine the kinetic parameters, as described above. This can serve as an additional tool for optimizing the process and operational parameters depending on the desired pellet quality.
7.2 Oxidation

The results from the oxidation experiments, firstly at particle scale to evaluate the corresponding oxidation kinetics, development of the mathematical model and contemplation of predicted oxidation behavior at pellet scale, are presented and discussed in this section.

7.2.1 Magnetite concentrate

7.2.1.1 Fraction and Rate of Oxidation

For the Fe₃O₄ content of the concentrate used in this study, the theoretical or maximum weight gain percentage (ΔW_{max}), that the magnetite particles can achieve during its oxidation to hematite is evaluated to be 3.46%. The fraction (f) or degree of oxidation is determined as the ratio of the weight gain captured by TGA to the maximum weight gain of the magnetite particles during oxidation, as mentioned in Equation (14). Thereafter, the oxidation rate related to the oxidation fraction is calculated for the given thermal profile.

\[
f = \frac{(W_f - W_i) \times 100}{\Delta W_{max}} = \frac{\Delta W_{TGA}}{\Delta W_{max}}
\]

where ΔW_{TGA} is the percentage weight change measured during oxidation in TGA between the initial weight (W_i) and final weight (W_f) of the particles.

The fraction of oxidation and rate of oxidation for the magnetite concentrate exposed to different temperatures, partial pressure of oxygen and size fraction, with respect to time are shown in Figure 16. It is observed that oxidation fraction increases initially at a rapid rate, and thereafter attains a plateau region where oxidation increases gradually at constant oxidation rate. This infers that the oxidation of magnetite at a particle scale is a two-step phenomenon, which is in line with the findings reported by several researchers\textsuperscript{9,12,102,103}. Oxidation fraction (f) is found to be increasing with temperatures from 773 to 1073 K (500°C to 800°C) as well as with the increasing p_{O₂} from 0.05 to 0.21, as shown in Figure 16 (a) and (b), respectively. Finer size fractions, having larger surface area, attains a higher degree of oxidation as compared to the relatively coarser particle size fractions, in the order of 38 to 53 μm > 53 to 63 μm > 63 to 74 μm, as shown in Figure 16 (c).
Figure 16: Oxidation Fraction and Oxidation Rate for magnetite particles with respect to (a) isothermal temperatures, (b) $P_{o_2}$ in oxidizing gas and (c) size fraction.
7.2.1.2 Estimation of Oxidation Kinetic Parameters

The isothermal oxidation fraction is further analyzed by the Shrinking Core mechanism and Avrami mechanism to describe the magnetite oxidation phenomenon and determine the kinetic parameters.

7.2.1.2.1 Shrinking Core Model (SCM)

According to SCM, the conversion proceeds by mass transfer of the gaseous phase, chemical reaction and solid-state diffusion kinetics, described in Equation (15). Generally, mass transfer of the oxidizing gas to the particle surface is not rate limiting; this is also true when the gas flow rate is optimized with the help of starvation tests in TGA. If the chemical reaction is the dominant step, the fractional conversion for the spherical particles with respect to time proceeds according to Equation (16), whereas, if diffusion through the product layer is the rate controlling mechanism, the same is represented by Equation (17) 95,102.

\[
\frac{r}{3k_m} f + \frac{r}{k_R} \left[1 - (1 - f)^{\frac{1}{3}} \right] + \frac{r^2}{6k_S} \left[3 - 2f - 3(1 - f)^{\frac{4}{3}} \right] = \frac{CM}{\rho_B} t
\]  

(15)

where, \( f \) is the fraction of conversion for concentrate comprising of particles with an average radii \( r \) for isothermal time \( t \), while \( k_m \), \( k_R \), and \( k_S \) are rate constant for mass transfer of gas, chemical reaction at the interface and diffusivity, respectively. \( M \) and \( \rho_B \) are molar mass and density of the reactant, respectively, whereas \( C \) is the concentration of oxygen in the reacting gas.

Chemical reaction at the interface, \( F_R = \left[1 - (1 - f)^{\frac{1}{3}} \right] = k_R t_R \)  

(16)

Diffusion through the product layer, \( F_S = \left[3 - 2f - 3(1 - f)^{\frac{4}{3}} \right] = k_S t_S \)  

(17)

where, \( F_R \) and \( F_S \) are conversion fractions corresponding to chemical reaction and diffusion in the isothermal time \( t_R \) and \( t_S \) with the rate constants \( k_R \) and \( k_S \), respectively.

Oxidation fraction of magnetite concentrate for different isothermal temperatures have been rearranged and plotted according to Equation (16) and (17) with respect to the time respectively, as shown in Figure 17. The fractional conversion vs time plots for the initial oxidation as well as the later stages (Figure 17(b)) fits a straight line equation, as shown in Figure 17(a) and (b), respectively. This infers that the oxidation of magnetite particles proceeds by SCM initially.
dominated by chemical reaction and thereafter by diffusion through the hematite product layer. The slopes of the curve determine the rate constant terms ($k_R$ and $k_D$), respectively.

Figure 17: Isothermal oxidation by Shrinking Core Model with respect to different temperatures, $pO_2$, and size fraction with (a) chemical reaction and (b) diffusion through product layer as dominant mechanisms.
Since, oxidation is also a thermally activated phenomenon, the variation in the rate constant with respect to isothermal temperature is expressed by the Arrhenius equation (Equation (8)) and plotted as shown in Figure 18 for each of the mechanism independently. The respective slope and intercept of Equation (8) determine the activation energies for the chemical reaction and diffusion for oxidation of magnetite particles, which are found to be 31 and 76.5 kJ/mol, respectively.

![Figure 18](image)

**Figure 18**: Arrhenius equation plots for estimating Activation energy for (a) chemical reaction and (b) solid state diffusion controlling mechanism

### 7.2.1.2.2 Avrami Kinetic Model (AKM)

Avrami Kinetic Model hypothesizes that the isothermal conversion or phase transformation of particles proceeds by nucleation and growth, represented by Equation (18). The results of isothermal oxidation from experiments on magnetite concentrate have also been analyzed with AKM by rearranging the Equation (18) in the form of a straight line as mentioned in Equation (19). The fraction of oxidation is plotted with respect to time according to Equation (19) for magnetite concentrate exposed to different temperatures, $p_{O_2}$ and size fraction, and are shown in Figure 19.

\[
\left( \ln(-\ln(1-f)) \right) = n \ln(t) + \ln(a) \tag{19}
\]
Figure 19: Isothermal oxidation by Avrami Kinetic Model (AKM) for different (a) isothermal temperatures, (b) partial pressure of oxygen and (c) size fraction.

It is found that there are two straight lines with different slopes corresponding to initial and later stages of oxidation for all the three variables. It also infers AKM fits the isothermal oxidation of magnetite concentrate satisfactorily.

Further, Avrami rate constant ($\alpha$) for different isothermal experiments is related to Arrhenius rate constant ($K$) according to Equation (20). This rate constant is further related to temperature by Arrhenius relation (Equation (8)), and is plotted for the nucleation and growth stages, as shown in...
Figure 20. Thereafter, activation energies ($Q$) and pre-exponential factors ($K'$) are estimated by evaluating the respective slopes and intercepts.

$$K = \alpha^n$$  \hspace{1cm} (20)

Figure 20 : Arrhenius plots for Avrami Kinetic Model (AKM) for (a) nucleation and (b) growth mechanisms during oxidation of magnetite concentrate

Activation energies estimated for nucleation and growth mechanisms are 15 and 226 kJ/mol, respectively. Therefore, it can be postulated that during oxidation, the hematite ($\text{Fe}_2\text{O}_3$) needles grow by solid-state diffusion into the matrix of magnetite ($\text{Fe}_3\text{O}_4$) particles\textsuperscript{103}. Although, there might exist some uncertainties in the first few seconds of the initial stage because of too few data points. Therefore, the analysis hereafter is focused primarily on the later stage of oxidation reaction to determine the kinetic parameters.

Pre-exponential factor ($K'$) is found to vary with $p_{O_2}$ and $d_p$ according to Equation (21) and (22), respectively. Whereas, the time exponent ($\eta$) is found to increase linearly with respect to the temperature and decreases with $p_{O_2}$ as per the Equation (23) and (24), respectively, while it does not vary with the size fraction ($d_p$) of particles.
7.2.1.3 Comparison of SCM and AKM – Isothermal Oxidation prediction

The kinetic parameters derived are used further to develop the model for magnetite concentrate by adopting both the abovementioned kinetic models, SCM and AKM. The predicted profiles for oxidation fraction \( f \) exposed to different temperatures with respect to time are validated with that measured from TGA experiments, as shown in Figure 21.

\[
K' = 2.81 \times 10^8 p_{O_2} + 7.511 \times 10^8
\]  
(21)

\[
K' = -6.054 \times 10^{13} d_p + 4.024 \times 10^9
\]  
(22)

\[
n = 4.938 \times 10^{-4} T - 0.197
\]  
(23)

\[
n = -0.428 p_{O_2} + 0.3231
\]  
(24)

Figure 21: Predicted and experimental isothermal oxidation of magnetite concentrate (38 – 53 μm) according to (a) Shrinking Core Model (SCM) and (b) Avrami Kinetic Model (AKM).

The figure shows that the oxidation profiles predicted from AKM (Figure 21(b)) are significantly in better agreement with the experimental observations as compared to those predicted from SCM (Figure 21(a)).
Further, the optical microstructures of magnetite particles (38 – 53 μm) which are oxidized at the isothermal temperature of 873 K (600°C) and 1073 K (800°C) for 60 minutes are examined, as shown in Figure 22. It is observed that the oxidation proceeds inwards from the surface of the magnetite particle by nucleation of needle-like hematite crystals which starts to grow in the magnetite along the preferred planes at the lower temperature (873 K (600°C)). Similar findings have been observed by Monazam et al.\textsuperscript{103}. As the extent or fraction of oxidation increases at higher temperatures (1073 K (800°C)), it seems that there is a sharp reaction interface which progresses inwards somewhat in an anisotropic manner albeit hematite needles grow significantly ahead of the reaction interface. A similar observation was reported by Monsen et al.\textsuperscript{58}. Thus, it can be substantiated that the oxidation of magnetite concentrate considered in this study proceeds by nucleation and the growth of hematite needles into magnetite particles occurs via solid-state diffusion mechanism. These findings are also consistent with particles exposed to different $p_{O_2}$ and $d_p$.

Furthermore, the values of activation energy estimated by the SCM in this study for diffusion stage is 76.1 kJ/mol. Activation energies in the similar range have been found by Cho\textsuperscript{102} by adopting the SCM. The cause for lower activation energies in regards to solid-state diffusion was attributed to the short-circuit path or grain boundary diffusion. Whereas, significantly higher activation energy values such as 242 kJ/mol, 208 kJ/mol, and 469 kJ/mol have been reported by Himmel\textsuperscript{111}, Päidassi\textsuperscript{112} and Davies\textsuperscript{113}, respectively, for the solid-state diffusion mechanism.
However, the activation energy determined by AKM for the growth stage in this study is 226 kJ/mol, which falls in the range reported in literature\textsuperscript{111-113}. Also, this inference is well backed up by the predicted profiles for oxidation fraction by AKM which agrees with those obtained experimentally (Figure 21). This hypothesis is also supported well by the microstructural observations of the growth of hematite needles ahead of reaction interface (Figure 22). Therefore, from the prospect of activation energy values, predicted oxidation profiles and microstructural observations, it is pursued that AKM suitably describes the oxidation mechanisms of magnetite concentrate. Hence, AKM is adopted for further predicting the oxidation behavior of magnetite concentrate.

7.2.1.4 Non-Isothermal Oxidation Prediction

The kinetic parameters derived from the isothermal investigation using AKM is extended to predict the non-isothermal oxidation behavior of magnetite concentrate. This has been done by discretizing the entire non-isothermal (time-temperature) plot with several small pseudo isothermal steps. The variation in oxidation fraction ($f$) can be obtained from the temporal variation of temperature and the corresponding Avrami coefficients ($n$, $K'$), using Equation (18) by progressing in time for the sufficiently small step of $\Delta t$.

In order to develop the oxidation model which should be capable to consider all the three parameters investigated as variables, the kinetic parameters ($n$, $K'$) have been correlated to obtain their combined effect. The Avrami time exponent ($n$) is a function of $T$ and $P_{O_2}$, whereas, the pre-exponential factor ($K'$) is dependent on $P_{O_2}$ and $d_p$. These coefficients are correlated to the variables in a bilinear way using least square fitting method according to Equation (25) and (26), respectively.

\[
n = 1.76 \times 10^{-4}T + 0.1255 \ln(P_{O_2}) - 2.03 \times 10^{-4}T \cdot \ln(P_{O_2}) \]  
\[
\log_{10}K' = 11.46 + 0.786 P_{O_2} - 5.55 \times 10^{-4}d_p 
\]  

Further, these predictions have been validated by the non-isothermal oxidation experiments. The predicted non-isothermal oxidation profiles have been plotted along with the experimental profiles for validation, and are shown in Figure 23.
The figure shows that there is a kink at approximately \( f = 0.55 - 0.65\% \) around the temperature of 723 K (450°C). Similar observations have been reported earlier\(^5,\text{14,15}\), and it has been postulated that it is due to the formation of \( \gamma\text{-Fe}_2\text{O}_3 \) (maghemite) at lower temperatures, and further to \( \alpha\text{-Fe}_2\text{O}_3 \) (hematite) at relatively higher temperatures (say 873 K (600°C)). However, the metastable nature of \( \gamma\text{-Fe}_2\text{O}_3 \) makes it difficult to substantiate by means of characterization. It is observed that the predicted oxidation profiles satisfactorily follow the experimental oxidation profiles with respect to the pattern or progress of oxidation curves. Although, it can also be inferred that there is a slight deviation from model predictions in regards to the absolute extent of oxidation fraction. The values of \( n, K' \), which significantly affects the oxidation behavior have been fine-tuned to estimate the range where predictions are statistically accepted. Optimizing these by least square fit enables to generate the non-isothermal oxidation predictions for entire thermal profiles within 90% confidence interval (CI).

The deviations from the experimental observations could be attributed to the fact that shape of particles within each narrow size fraction is not uniform and spherical. Another limitation could be because of the lack of experiments at different temperatures for the range of \( p_\text{O}_2 \) and \( d_\text{p} \) while...
determining the kinetic parameters. Although these experiments are not in this scope of study, incorporating them will increase the window of experimental observations which could improve the model efficiency. In future, the particle kinetics and model demonstrated will be utilized to upscale and develop the oxidation model for magnetite at pellet scale.

7.2.2 Magnetite Pellet

7.2.2.1 Model Formulation (Grain Model)

The concept of a grain model for gas-solid reaction system is utilized to develop the model for oxidation kinetics of magnetite pellet. The rate of oxidation at the particle scale depends on the estimated kinetic parameters as well as the local concentration of oxidizing gas inside the pellet\(^{95,100,106}\). Therefore, the overall oxidation model is developed by adopting the kinetics of diffusion of oxidizing gas through pores, particle oxidation, and associated heat transfer, in this sequence. While developing the model, it is assumed that the pellet is made up of several spherical magnetite particles. The magnetite pellet also contains the particles of bentonite (binder) but they are assumed to be neglectable i.e. they do not participate in any reaction or influence oxidation of magnetite.

7.2.2.1.1 Pore Diffusion Kinetics

The oxidation of particles in the pellet is dependent on the diffusion kinetics of the oxidizing gas through the pores, and thus the mole fraction of oxygen \(X_{O_2}\) across the radial position in the pellet. As the oxygen diffuses inward, it gets consumed by the particles for oxidation, and hence, the \(X_{O_2}\) decreases continuously. The output \(X_{O_2}\) from the magnetite particles is input to the subsequent magnetite particles further into the pellet. The extent to which the oxygen diffuses in the pellet at the particular temperature and reaction time defines the inward progression of the oxidation front at the pellet scale.

The diffusion flux of \(O_2\) \((\dot{N}_{O_2})\) from the oxidizing gas comprised of \(O_2\) and \(N_2\) inside the pellet\(^{116}\):

\[
\dot{N}_{O_2} = -C D_{eff} \frac{d}{dr} X_{O_2} + X_{O_2} (\dot{N}_{O_2} + \dot{N}_{N_2})
\]  \hspace{1cm} (27)

where \(D_{eff}\) is the effective diffusivity of the oxidizing gas, \(C\) is the molar concentration of oxidizing gas, \(X_{O_2}\) is the mole fraction of \(O_2\), \(\dot{N}_{O_2}\) and \(\dot{N}_{N_2}\) are the diffusive flux of \(O_2\) and \(N_2\) in the oxidizing gas, respectively.
Since, $N_{N_2} = 0$, therefore **Equation (27)** is written as in **Equation (28)**.

$$
N_{O_2} = \frac{-D_{eff} C}{1-X_{O_2}} \frac{dX_{O_2}}{dr}
$$

**Equation (28)**

The effective diffusivity of the oxidizing gas in the pellet is a function of porosity ($\varepsilon$) and tortuosity ($\tau$) of the pellet, as mentioned in **Equation (29)**.

$$
D_{eff} = D_{O_2-N_2} \left( \frac{\varepsilon}{\tau} \right)
$$

**Equation (29)**

where $D_{O_2-N_2}$ is the diffusion coefficient of the oxidizing gas.

The consumption of oxygen during its excursion through the pellet pores can be determined by the conservation of flux for the $O_2$, according to **Equation (30)**,

$$
\frac{1}{r^2} \frac{d}{dr} \left( r^2 N_{O_2} \right) - G(r) = 0
$$

**Equation (30)**

The corresponding boundary conditions for $O_2$ diffusion are,

at $r = R$, $N_{O_2} = k_{O_2} C(X_{O_2, surface} - X_{O_2, bulk})$ and, at $r = 0$, $\frac{dX_{O_2}}{dr} = 0$

$$
\dot{G}(r) = \left( \dot{N}_p \right) \delta_{M,FeO_4} \left( 0.25 \right) \frac{df}{dt}
$$

**Equation (31)**

$$
\dot{N}_p = \frac{(1-\varepsilon)}{2(\pi d^2)}
$$

**Equation (32)**

where $\dot{G}(r)$ is the number of moles of $O_2$ consumed at any radial location $r$ per unit volume of pellet per unit time and $\dot{N}_p$ is the number of particles per unit volume of the pellet.

### 7.2.2.1.2 Oxidation Kinetics of Particles

As it is found earlier that the oxidation kinetics of magnetite particles suitably follows the Avrami mechanism, represented by **Equation (18)**, the rate of oxidation of particles locally at any location across the pellet depends on $X_{O_2}$, that has been diffused to the individual particle surface, according to **Equation (33)**.
\[
\frac{df}{dt} = n a e^{-at^n} t^{n-1}
\] (33)

The oxidation of individual particles are expected to be affected by the local temperature in the pellet in an Arrhenius manner according to Equation (8) and are correlated with Avrami mechanism by Equation (19) and (20). The derived kinetic parameters \((n, K', \text{ and } Q)\) are related to the process variables \((T_p, \alpha, \text{ and } d_p)\) according to Equation (25) and (26). Thereafter, the principle of superposition is used to determine the rate of oxidation under isothermal conditions as discussed earlier.

7.2.2.1.3 Heat Transfer

The heat transfer within the pellet is modelled using one-dimensional conduction equation (Equation (34)) given below,

\[
\rho c_p \frac{dT}{dt} = \frac{1}{r^2} \frac{d}{dr} \left( r^2 k_{\text{eff}} \frac{dT}{dr} \right) + \dot{H}_{\text{Gen}}
\] (34)

Here, \(k_{\text{eff}}\) is the effective conductivity of the pellet and \(\dot{H}_{\text{Gen}}\) is the exothermic heat generation due to local rate of oxidation.

Initially, the whole pellet is at ambient temperature, \(t = 0, 0 < r < R, T = T_{\text{ambient}}\)

As the pellet is lowered into the furnace, the furnace temperature is assumed to be changing linearly. In the isothermal (hot) zone of the furnace, the furnace temperature is constant. The heat transfer to the pellet is primarily governed by radiative heat transfer. This is incorporated into the boundary condition, which can be written as Equation (35).

\[
-k_{\text{eff}} \frac{dT}{dr} \bigg|_{r=R} = \sigma \varepsilon (T_{R=R}^4 - T_{furnace}^4)
\] (35)

The effective thermal conductivity \((k_{\text{eff}})\) used here is determined from experiments on thermal diffusivity \((\alpha)\) measurements on magnetite green pellets using Laser Flash technique derived from the work done by Andersson and Björkman\(^{116-118}\).
7.2.2.2 Model Predictions

After formulating, the model is used to run with the input parameters mentioned in Table VI to examine the predicted oxidation behavior of magnetite pellet under different thermal and gaseous conditions with that measured experimentally in TGA.

Table VI: Input Parameters to the Pellet Oxidation Kinetic Model

<table>
<thead>
<tr>
<th>Particle Variables</th>
<th>Pellet variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Particle Size</td>
<td>Size of the pellet</td>
</tr>
<tr>
<td>35 X 10^-6 m</td>
<td>10 X 10^-3 m</td>
</tr>
<tr>
<td>Maximum weight gain for Fe3O4 particles during oxidation</td>
<td>3.455%</td>
</tr>
<tr>
<td>Magnetite Oxidation heat</td>
<td>Partial pressure of O2 in the oxidizing gas</td>
</tr>
<tr>
<td>460 kJ/mol</td>
<td>0.15 atm</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>0.21 atm</td>
</tr>
<tr>
<td></td>
<td>0.30 atm</td>
</tr>
<tr>
<td></td>
<td>1.00 atm</td>
</tr>
<tr>
<td></td>
<td>Initial temperature of the pellet</td>
</tr>
<tr>
<td></td>
<td>300 K</td>
</tr>
<tr>
<td></td>
<td>Surrounded or Furnace temperature</td>
</tr>
<tr>
<td></td>
<td>873 K (600°C)</td>
</tr>
<tr>
<td></td>
<td>973 K (700°C)</td>
</tr>
<tr>
<td></td>
<td>1073 K (800°C)</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity for magnetite pellet</td>
</tr>
<tr>
<td></td>
<td>1.5 W/m/K</td>
</tr>
<tr>
<td></td>
<td>Emissivity of magnetite pellet (reasonable to assume near black)</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Mass Transfer coefficient across the pellet</td>
</tr>
<tr>
<td></td>
<td>1.02 X 10^-2</td>
</tr>
<tr>
<td></td>
<td>Number of cells in the pellet</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Time interval in each cell</td>
</tr>
<tr>
<td></td>
<td>0.01 sec</td>
</tr>
<tr>
<td></td>
<td>Holding time at isothermal temperature</td>
</tr>
<tr>
<td></td>
<td>3600 sec</td>
</tr>
</tbody>
</table>

7.2.2.2.1 Oxidation Fraction and Oxidation Rate for the Pellets

The overall oxidation fractions and oxidation rates with respect to time for the magnetite pellets exposed to different temperatures and partial pressures of oxygen in the oxidizing gas are predicted from the pellet oxidation model and are shown in Figure 24. The predicted profiles are compared with those obtained from the oxidation experiments for pellets conducted in the TGA. The weight gain during the oxidation of magnetite pellets is converted to their corresponding fraction of oxidation \( f_{TGA} \) by equating with respect to the theoretical weight gain, according to Equation (14). The theoretical or maximum weight gain \( \Delta W_{max} \) evaluated for the pellets during oxidation
of magnetite to hematite used in this study is 3.36%, which accounts for the weight loss associated with the bentonite.

The oxidation fraction of pellet increases at a rapid rate initially to the major extent and thereafter increases gradually at the slow rate once it reaches the plateau region as shown in Figure 24 (a), similar to that observed for magnetite particles. Overall, the oxidation fraction is found to be increasing with temperatures, whereas, it tends to attain similar extent with increasing $p_{O_2}$ at the same temperature. The predicted profiles for oxidation fraction is in fair agreement at 873 K (600°C) in comparison to that determined from TGA experiments. Whereas, it is over-predicting at higher temperatures where oxidation fraction increases with temperature from 973 to 1073 K (700 to 800°C) at $p_{O_2}$ of 0.21 atm. The predicted oxidation profiles for pellets exposed to different $p_{O_2}$ at 873 K (600°C) are also in fine agreement as compared to that obtained from TGA experiments, with the exception at $p_{O_2}$ of 1.00 atm, where it is over-predicted.

Unlike the particle oxidation behavior, the rate of oxidation with time obtained from the TGA experimental data shows interesting behavior; two peaks at high temperatures and at lower temperatures the second peak evolves to a plateau, as depicted in Figure 24 (b). This type of behavior either has not been reported or discussed for magnetite pellet oxidation in the previous studies. The model is able to capture this behavior. Though a similar behavior with oxygen partial pressures is also observed in the experimental rates of oxidation, the model has captured this behavior only to a limited extent.

In order to analyze the possible reasons for this behavior, simulation experiments were conducted. When simulations are carried out with pellet being at the furnace temperature from the start of oxidation (please note that experimentally this was not possible, as the pellet is lowered to the high temperature zone), the rate of oxidation shows a monotonic decrease in rate of oxidation with increasing time. The thermal conductivity of the pellet did not show significant variation in the rate of oxidation curves. Simulation experiments carried out without considering the heat of oxidation showed significant decrease in peaks intensity though the shapes of the curves remained similar. However, simulation experiments with changing diffusivity of oxygen, mass transfer coefficient and pre-exponential factor for the particle kinetics changed the oxidation curves significantly. It may note that particle oxidation kinetics showed a large initial rates followed by sharp decrease in rates at higher extents of oxidation. Similarly local temperature variation due to oxidation heat can also change the rates of oxidation significantly. These effects in conjunction with diffusion of oxygen results in such non-monotonic behavior. It should be also noted that the effect of oxygen partial pressures on the particle oxidation kinetics has been experimentally obtained only for a single temperature. Possibly, more experiments on particle oxidation varying the oxygen partial pressure and temperatures can give better predictions on the pellet scale.
Figure 24: Overall oxidation fraction and oxidation rate profiles predicted by Pellet Oxidation Model for (a) three temperatures levels and (b) four levels of partial pressure of oxygen in oxidizing gas for magnetite pellets and compared with those obtained from TGA experiments.

However, it is observed from the Figure 24 (b) that there exists the deviation between the predicted and experimental oxidation rate curves. It is to be noted that the magnetite pellet chosen in this study for the TGA experiments consists of multi-sized particles in the desired proportion. Hence, the finer sized particles within the pellet oxidize at the rapid rate with respect to the coarser particles. It is therefore postulated that the presence of fine particles in the pellet increases the
oxidation rate in the experiments as compared to that of the predicted one with mono-sized particles.

7.2.2.2 Microstructural Inspection

Further, in order to affirm the understanding, the microstructural investigation is performed both at pellet scale and particle scale. For this purpose, the interrupted oxidation tests for magnetite pellets are been designed in such a way that it can help in tracking the progress of oxidation front at pellet as well as particle scale.

The mosaic optical microstructures of partially oxidized magnetite for 120 and 480 secs are captured at the pellet scale across the radial distance from the surface to the center of pellet, as shown in Figure 25. It can be seen that the pellet oxidation front observed has progressed farther into the pellet in both time intervals, whereas, the particle oxidation front has not yet reached to the center of the particles. This infers that the oxidation front at pellet scale and the particle scale travels at different rates. It seems that the diffusion of oxygen gas is limited beyond the pellet oxidation front, and hence, the particles did not start to oxidize. However, fine particles at the surface of the pellet are either completely oxidized or have reached to the significant extent as compared to the relatively coarser particles. This substantiates the findings postulated from the oxidation rate curves from TGA experiments as well as predicted from the pellet oxidation model.

The oxidation kinetic model developed in this study is further used to predict the progress of the oxidation of magnetite at the pellet scale across the radial distance. According to the output from the pellet oxidation model, it is proposed that the complete and homogeneous oxidation of magnetite pellets can be obtained either by elevating the oxidation temperature to 973 K – 1073 K (700°C – 800°C) or by enriching the oxygen (60% or 100% O2) in oxidizing gas or by the combination of both.
Figure 25: Optical Microstructure of partially oxidized pellet quenched after (a) 120 sec and (b) 480 sec at 973 K (700°C) and $p_{O_2} = 0.21$ atm at pellet scale and at particle scale across the radial distance at the magnification of 1000 x
8 Conclusions

The phenomena responsible for physico-chemical changes during induration of magnetite pellet, namely – sintering and oxidation, have been successfully investigated in this study. These phenomena were quantified independently by carefully designed experiments on the single pellets. The kinetic parameters, $\eta$, $K'$ and $Q$, necessary to describe any phenomena were estimated by appropriate analysis and subsequently developed the sintering and oxidation models. The findings from the current investigation are briefly presented below:

- An optical dilatometer is successfully used to capture the shrinkage, and hence sintering of the pellet. Sintering of oxidized magnetite pellets estimated the value of $\eta$ to be 0.22, while activation energy is 509 kJ/mol over the range of sintering temperatures (1373 – 1623 K (1100 – 1350°C)). This suggests that there exists a single dominant mechanism during sintering of oxidized magnetite pellets. Sintering of non-oxidized magnetite pellets shows that the value of $\eta$ 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/mol at lower temperatures (1173 – 1373 K (900 – 1100°C)) and higher temperatures (1373 – 1623 K (1100 – 1350°C)), respectively, suggesting the possibility of two distinct mechanisms. The extents of sintering have been predicted under non-isothermal conditions as well by incorporating the variations in the above mentioned kinetic parameters ($\eta$, $K'$ and $Q$), with temperatures, for both oxidized and non-oxidized magnetite pellets, and are validated using experimental data.

- A novel methodology to digitize the microstructural images of the sintered pellets has been developed, and establishes correlation between the macroscopic and microscopic features during the sintering phenomena in pellets (porous powder compacts). In this context, optical microstructures of oxidized and non-oxidized magnetite sintered pellets were quantitatively characterized for the sintering degree by the application of distance transform principle. The sintering degree at microscopic scale was successfully estimated, and the trends were consistent with those obtained from macroscopic investigations. In the future, this method could be further extended to correlate the pellet quality (mechanical and metallurgical properties) and develop an online tool to assist in optimizing the process and operational parameters.

- Further, the oxidation behavior of magnetite has been successfully investigated quantitatively at particle scale using TGA. Experimental results have been analyzed by two kinetic models, namely, Shrinking Core Model (SCM) and Avrami Kinetic Model (AKM), and the latter was found to describe the oxidation phenomenon of magnetite particles more suitably. It postulates that the oxidation at particle scale proceeds by nucleation and growth at initial and later stages, respectively, where the growth is by diffusion mechanisms. This was also substantiated by microstructural examination of individual particles, where hematite needles were growing ahead of reaction interface into the magnetite. AKM is used to predict oxidation behavior for magnetite concentrate under non-isothermal conditions, and validated by TGA experiments.
The Pellet Oxidation Model has been developed on the approach outlined by the Grain Model for gas-solid reaction kinetics, by incorporating the Avrami Kinetic Model for oxidation kinetics at particle scale. The simulated oxidation fraction and oxidation profiles were well complimented by those determined experimentally at pellet scale in TGA in the range of temperature and partial pressure oxygen in oxidizing gas considered. The experiments showed that the oxidation rate curves possess two peaks with the peak intensity increases with temperature, whereas they marginally increase with respect to the partial pressure of oxygen. The same has been complemented well by the results predicted from the pellet oxidation model.

Additionally, the model is used to predict the progress of oxidation front into the pellet which is exposed to different temperature and oxygen levels in the oxidizing gas. It is found that when the magnetite pellet is oxidized at the temperature of 973 K – 1073 K (700°C – 800°C) at 21% O₂ or by enriching the oxygen levels (60% or 100% O₂) at 1073 K (800°C) or by the combination of both can achieve complete oxidation in the minimum possible time.

In the end, it is concluded that Sintering and Oxidation models have been successfully developed to capture the physico-chemical transformations at the scale of single pellet during induration of magnetite. Additionally, it is intended in future to integrate the oxidation and sintering models to develop the overall comprehensive Single Pellet Induration Model (SPIAM) for magnetite pellet.
9 Future Work

With the objective of modeling the physico-chemical transformations of magnetite pellet during induration process; following are the steps ahead for future work in succession to the findings obtained in the current study:

- Incorporate the effect of multi-sized particle distribution at each cell layer into the pellet oxidation model. This will help in refining the model and further improves its efficiency.

- Oxidation kinetics at particle scale are very sensitive, hence to improve the oxidation model, particle experiments have to be done at varying oxygen levels at different temperatures and similarly with size fraction.

- Kinetic parameters estimated for oxidation (of magnetite) and sintering (of oxidized magnetite and non-oxidized magnetite) phenomena in isolation, will be integrated together to develop a mathematical model simulating the overall induration process of magnetite pellet (SPIM). The model developed will be validated by single pellet experiments exposed to the complete induration profile at different temperatures, heating rates and oxygen content in the oxidizing gas.

- Further, the proposed SPIM can be extended to incorporate the variables, such as pellet size, different additives, etc. by careful experimentation. This refines the model and makes it more robust widening the range of its application.

- Quantify the morphology of the pellets by automated image analysis to derive the degree of oxidation and sintering, and validate with that found experimentally at the macroscopic level.

The model for predicting induration behavior of magnetite pellet will provide an effective aid to the furnace operator, and helps in designing the optimum operating profile to achieve the desired pellet quality and improving the productivity. It can also be very useful to design the operating profile considering the variability in the raw material mix in the future.
Bibliography


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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 are not only dependent on the thermal and gaseous environment the pellet gets exposed to in the induration reactor but also interdependent on each other. Therefore, a systematic study should involve understanding these processes in isolation to the extent possible and quantify them seeking the physics. With this motivation, the present paper focuses on investigating the sintering kinetics of oxidized magnetite pellet. For the current investigation, sintering experiments were carried out on pellets containing more than 95 pct magnetite concentrate from LKAB’s mine, dried and oxidized to completion at sufficiently low temperature to avoid sintering. The sintering behavior of this oxidized pellet is quantified through shrinkage captured by Optical Dilatometer. The extent of sintering characterized by sintering ratio found to follow a power law with time (i.e., \(K^n\)). The rate constant \(K\) for sintering was determined for different temperatures from isothermal experiments. The rate constant, \(K\), varies with temperature as \(\ln(K/T^n) = \ln K - Q/R T\), and the activation energy (\(Q\)) and reaction rate constant (\(K\)) are estimated. Further, the sintering kinetic equation was also extended to a non-isothermal environment and validated using laboratory experiments.


I. INTRODUCTION

Iron ores becoming leaner necessitate beneficiation at finer scales. Globally, this has led to growth in pelletization as an agglomeration process. In addition, pelletization of steel plant solid wastes enables them to be used in various iron and steel processes. Pelletization has been widely practiced for magnetite ores, as it offers an added advantage in terms of energy generated from the oxidation of magnetite to hematite. In Sweden, pelletization is the most important agglomeration process used industrially. Swedish steel industries have stopped using the other widely used agglomeration process—sintering altogether and have pioneered in operating blast furnaces with cent percent pellets.

Magnetite ore grounded and beneficiated to an appropriate grade and size distribution is mixed with binder and agglomerated into spherical balls in a disk or drum pelletizer. The green pellets are strengthened through heat hardening process known as induration 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. In straight grate, green pellets form a packed bed that is continuously moved through a long furnace. The hot gases are allowed to flow upward as well as downward through the packed bed for efficient heat transfer. In case of rotary Kiln process, partially processed pellets from a straight grate furnace are processed further in a rotating drum furnace. Pellet quality primarily measured in terms of strength and reducibility depends on the excursion the pellet makes through the thermal and gaseous environment in the induration furnace.

During induration, magnetite pellets undergo primarily drying, oxidation and sintering. Among these processes, drying almost gets completed at about 373 K (100 °C). Some of the chemically bonded water may not get released until the pellet temperature reaches 523 K (250 °C).1 At higher temperatures, primarily oxidation of magnetite and strengthening (sintering) occur.

Ideally for a good pellet quality, the oxidation of the pellet should be followed by sintering of the oxidized...
magnetite grains. The oxidation determined by the intrinsic oxidation kinetics and diffusion of gases through the pores of the pellet proceeds from the pellet surface to the interior. This oxidation process is an exothermic process that generates heat within the pellet and can result in non-uniform temperature within the pellet. Simultaneously, the sintering of the oxidized magnetite (hematite) grains as well as the non-oxidized magnetite grains is initiated depending on the temperature and the sintering kinetics. It has been found that sintering of magnetite grains starts at much lower temperatures than that of hematite grains. Sintering, leading to a reduction of pore volume, adversely affects the oxidation phenomena. The interaction between oxidation, sintering, and the associated heat transfer can result in so-called duplex structure with a non-oxidized magnetite core with an oxidized shell. This interrelationship between various phenomena depends on the rate of these individual processes which in turn is determined by the processing conditions and the initial raw material.

In order to predict and quantify these physico-chemical phenomena during induration, a project has been initiated jointly by Lulea University of Technology (LTU) and Luossavaara-Kirunavaara AB (LKAB). At present, models at the reactor scale exist for predicting the overall performance of the induration furnace. However, their ability to predict the quality of the pellets and its distribution is very limited. For realizing these objectives, it is important that the physico-chemical phenomena are quantitatively described at the pellet scale and subsequently can be used as an input to the models at the reactor scale. The methodology adopted is to study each of the aforementioned phenomena in isolation to the extent possible, quantify them and further integrate them through modeling techniques to understand the interaction among these phenomena. Such model can provide (1) building blocks for reactor scale models to predict pellet quality as a function of process parameters and (2) correlate the raw material quality in terms of content, additions, size distribution, etc., to the induration process and pellet quality. These can help in designing process parameters for new grades of raw materials as well as improving existing processes. Sintering is one of the important phenomena during induration processes. The objective of this paper is to quantify the sintering of oxidized magnetite (hematite) pellet using optical dilatometer by deducing the kinetic parameters. Subsequently, the deduced kinetic parameters are validated with further experiments. Sintering kinetics of non-oxidized magnetite pellet will be presented in a future communication.

Powder metallurgists have been investigating sintering kinetics of the powder compacts of metallic and ceramic powders for many years. The extent of sintering of the powder compact is monitored through shrinkage measured using contact dilatometer. Numerous experiments have been reported on sintering studies on ceramic materials such as alumina, barium titanate, zirconia, uranium oxides, thorium oxides, etc., as well as metallic materials such as Ti, Fe, Zr, stainless steel, etc. Traditionally, dilatometric measurements have been performed on briquettes having an alumina push-rod to quantify shrinkage. The push-rod measures the linear displacement and cannot account for 3-D or 3-D spatial changes. A recent development by Expert System Solutions (ESS), Italy—Optical Dilatometer has facilitated to measure the dimensional variations solely on their optical images without having any contact with the sample. It works on principle of monitoring the periphery of the sample captured by two digital cameras equipped with high magnification and long working distance optical systems. Karamanov et al. compared the sintering kinetics estimated with the help of traditional push-rod dilatometer to that using the optical dilatometer. They found significant difference between these two measurements. They attributed the difference to the additional force exerted by the alumina push-rod over the sample contributing to its shrinkage. In this paper, a method to capture shrinkage of spherical pellets of approximately 10-mm diameter using Optical Dilatometer is established with an in situ measurement of area variation during sintering. This helps in assessing the shrinkage in 2-D. Any inhomogeneity in the green pellet can potentially get reflected in the shrinkage measurements.

Sintering is a complex process involving transport of species through various paths, such as bulk diffusion, surface diffusion, transport through the gaseous phase, etc., driven primarily to reduce the total surface energy. Most of the studies in ceramic and metallic powder processing were focused in finding the predominant mechanisms operating at different extents of sintering and sintering temperatures. Sintering studies on iron ore to deduce their kinetics have been relatively less. It can be noted that unlike conventional powder processing where the objective is to achieve close to 100 percent densification, in iron ore sintering, the objective is only to achieve sintering enough to provide sufficient strength during handling and subsequent operation in blast furnace and other reactors. At the same stage, sufficient porosity within in the pellet is necessary to achieve reduction in least time. Thus, sintering mechanisms responsible during the initial stages are only important for iron ore sintering. Wynnyckyj and Fahidy made an early in-road by studying the sintering kinetics of pure hematite reagent powder and commercial magnetite concentrate in the form of briquettes under isothermal conditions. They proposed a power law relation with time for isothermal sintering based on similar studies on sintering of metallic minerals and the same has been used in the present study. This model is described in detail at a later section. Interestingly, authors could not find any further quantitative studies either on magnetite or hematite sintering, though dilatometer measurements have been used to study sintering behavior.

II. EXPERIMENTAL DETAILS

A. Raw Material

The raw material chosen for the study was a concentrate from LKAB’s Malmberget mine. It was preserved
The pellets were characterized for their moisture content, true density, bulk density, and porosity. The known amount of green pellets were crushed and then placed into the Moisture Analyzer. Moisture analyzer completely evaporates the moisture by heating the sample overnight at 378 K (105 °C) and measures the weight loss. True density (skeletal density) of the single pellet as a whole was measured by AccuPyc II 1340 (Micromeritics Inc.) using 10 cm³ cell volume, the pycnometer which uses helium gas as displacement medium having an accuracy of 99.95 pct. The measurement of bulk density was tricky, as the use of commonly practiced Sand Flo pycnometer GeoPyc 1360 (Micromeritics Inc.) or Mercury Porosimeter would contaminate the surface of the pellet making it unsuitable for further processing. Therefore, use of tailor made light table imaging (LTI) was explored to measure the bulk volume of the pellet to determine its bulk density without harming the pellet surface. LTI is a set-up comprising high illumination light source, a horizontal tube furnace (100 mm in length and 20 mm in diameter) which can go up to maximum of 1873 K (1600 °C) with a sample stage and an image capturing microscope with recording facility. It is equipped with double-beam optical measuring system having two lenses attached to the image capturing device—one compatible for small samples (2 to 5 mm diameter) whereas other for bigger samples (6 to 12 mm diameter). The microscope transfers the image of the sample in the furnace at 5x magnification through a quartz window and onto the recording camera. The pellet sample is placed on a small alumina plate (15 × 15 mm²) resting on a thermocouple to measure the pellet temperature. It also has the provision for controlled in and out flow of the gases which maintains a constant flow across the pellet. The entire set-up is assembled to a computer system facilitated with specific Misura Thermal Analysis software to acquire and store the images of pellet subjected to a thermal profile, at predetermined time or temperature intervals. These images were processed to determine for area change as function of time during experiment.

D. Oxidation

Magnetite pellet was well-nigh completely oxidized to hematite by placing them in a chamber furnace. During oxidation, pellet gains weight corresponding to degree of oxidation of 90 pct or more. The optimum oxidation temperature and holding time were obtained by performing experiments from 873 K to 1073 K (600 °C to 800 °C) at different time intervals over the period of 24 hours, and found them to be 1023 K (750 °C) and 4 hours, respectively. After achieving 90 pct oxidation at 1023 K (750 °C), the pellet does not undergo any substantial oxidation even after a prolonged holding time of 24 hours [87 to 97 pct when held for 2 to 24 hours, respectively, at 1023 K (750 °C)]. At temperatures lower than 1023 K (750 °C), the oxidation degree is very low whereas at higher temperatures sintering may happen, both of which was not desirable. The pellets were then allowed to cool to room temperature, and then transferred to optical dilatometer for subsequent processing.

E. Sintering

Sintering studies are performed on these oxidized magnetite pellets. Sintering captured in terms of shrinkage through a horizontal contactless optical dilatometer (Misura® HSM-ODHT), schematic of which is shown in Figure 1. It was programmed to measure area change as opposed to linear change by push-rod dilatometer. It comprises of three principal units mounted on an optical bench: a continuously illuminated halogen light source, a horizontal tube furnace (100 mm in length and 20 mm in diameter) which can go up to maximum of 1873 K (1600 °C) with a sample stage and an image capturing microscope with recording facility. It is equipped with double-beam optical measuring system having two lenses attached to the image capturing device—one compatible for small samples (2 to 5 mm diameter) whereas other for bigger samples (6 to 12 mm diameter). The microscope transfers the image of the sample in the furnace at 5x magnification through a quartz window and onto the recording camera. The pellet sample is placed on a small alumina plate (15 × 15 mm²) resting on a thermocouple to measure the pellet temperature. It also has the provision for controlled in and out flow of the gases which maintains a constant flow across the pellet. The entire set-up is assembled to a computer system facilitated with specific Misura Thermal Analysis software to acquire and store the images of pellet subjected to a thermal profile, at predetermined time or temperature intervals. These images were processed to determine for area change as function of time during experiment.

### Table I. Chemical Composition of Raw Materials

<table>
<thead>
<tr>
<th>Concentrate (wt pct)</th>
<th>Bentonite (wt pct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>71.06</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.3943</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1198</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2586</td>
</tr>
<tr>
<td>Fe₂O₃ + K₂O</td>
<td>0.078</td>
</tr>
</tbody>
</table>

concentrate contains Fe₃O₄ >95 pct with Al₂O₃ and SiO₂ <0.6 and 7 pct moisture by weight, as mentioned in Table I. The magnetite ore was ground in the open grinding circuit in ball mills in three stages to produce concentrate identified as Malmberget pellet concentrate (MPC) having fineness of 65 pct passing through 45-μm screens and specific surface area ~9900 cm²/gm.

B. Balling

The concentrate was adjusted for humidity and then mixed with 0.5 pct dosage of bentonite as binder in a laboratory mixer (Eirich R02). This green mix of 7 kg was then fed to drum pelletizer (micro-balling) of 0.8-m diameter. Nucleation seeds of 3.5 to 5 mm were prepared first and subsequently balled into green pellets. The green pellets of desired size fraction of 9 to 10 mm were collected by screening. The smaller size of the green pellets than the widely used industrial average size (10 to 12 mm) for feeding into iron making units was decided based on the sample size limitations in the optical dilatometer (explained later). The green pellets were dried in oven at 423 K (150 °C) overnight, and stored in a desiccator for experiments.[37]
Pellets in all the experiments were exposed to a thermal profile of 50 K/min from room temperature to 1073 K (800 °C), and then at 30 K/min to the desired sintering temperatures as per experimental design mentioned in Table II, and holds at that temperature for 20 min. Experiments have also been conducted at different heating rates of 15, 30, 45 K/min reaching up to 1573 K (1300 °C) and subsequently holding the pellets isothermally for 20 min for the purpose of validation. Thereafter, the pellet was furnace cooled. A constant air flow rate has been maintained across the pellet in the furnace, so as to have sufficient oxygen available inside the furnace at any stage of sintering to avoid the dissociation of hematite back to magnetite. As the maximum flow rate specified for the optical dilatometer is 0.5 L/min, authors have used 0.3 L/min throughout which is within the maximum permissible limits. It has also been found that there is negligible change in weight before and after sintering assuring that the flow rate is optimum. The shadow images were captured continuously at an interval of 15 seconds to observe the shrinkage during sintering.

### III. RESULTS AND DISCUSSION

#### A. Degree of Sintering and Sintering Rate

A typical plot showing the percentage area change, \( \Delta A_{\text{percent}} = \frac{A_f - A_0}{A_0} \times 100 \) for a pellet with respect to time following a thermal profile obtained is shown in Figure 2. It should be noted that ‘A’ refers to projected area of the pellet at any instant of time and ‘A’ refers to that at the start of the experiment. In these experiments, it has been assumed that the temperature of the pellet at any instant of time is uniform within whole pellet. In order to confirm this, preliminary experiments were conducted by embedding thermocouples at the center and at the surface of the pellet to measure the difference between surface and center temperatures, respectively, during heating of the pellet in a furnace. It did not show any significant difference at the center and the surface temperatures. This showed that the characteristic time for the center temperature to reach the surface temperature is very small as compared to that of sintering process. Therefore, it is reasonable to assume that the pellet has a uniform temperature throughout. These findings were also supported through analytical heat transfer calculations.

As shown in Figure 2, the pellet expands initially during induration, and after reaching a maximum it begins to shrink under the influence of thermal profile. Pellet undergoes thermal expansion, and once the temperature reaches around 1273 K (1000 °C), the sintering phenomena dominates resulting in overall shrinkage of the pellet. Shrinkage in the isothermal segment is due to sintering alone, and thereafter during cooling, the pellet continues to shrink because of thermal contraction as well.

---

**Table II. Experimental Design to Study Sintering Kinetics of Oxidized Magnetite**

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Sintering Temperature [K (°C)]</th>
<th>Heating Rate [above 1073 K (800 °C)] [K/min (°C/min)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1423 (1150)</td>
<td>30</td>
</tr>
<tr>
<td>P2</td>
<td>1473 (1200)</td>
<td>30</td>
</tr>
<tr>
<td>P3</td>
<td>1523 (1250)</td>
<td>30</td>
</tr>
<tr>
<td>P4</td>
<td>1573 (1300)</td>
<td>30</td>
</tr>
<tr>
<td>P5</td>
<td>1623 (1350)</td>
<td>15</td>
</tr>
<tr>
<td>P6</td>
<td>1573 (1300)</td>
<td>45</td>
</tr>
<tr>
<td>P7</td>
<td>1573 (1300)</td>
<td>45</td>
</tr>
</tbody>
</table>
Thus, the overall change in size of the pellet is due to the combination of the thermal expansion/contraction and the sintering phenomena. 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.

For this, 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 (1000 °C) pellet begins to shrink non-linearly. During cooling also, the pellet shrinks linearly once the temperature reaches sufficiently low temperatures that the sintering is insignificant. The slopes of these linear variations both during heating and cooling are equal.

The volumetric thermal coefficient of expansion by its definition is given by:

\[ \alpha = \frac{1}{V} \frac{dV}{dT}. \]  

[1]

By integration,

\[ \left( \frac{\Delta V}{V_0} \right) = \exp(\alpha(T - T_0)) \approx 1 + \alpha(T - T_0) \]

(Reasonable approximation for \( \alpha \ll (T - T_0) \))

or \( V - V_0 \approx \alpha(T - T_0) \).

[2]

In the above, \( V_0 \) is the initial volume of a material at temperature \( T_0 \) and \( V \) is volume of the material at any temperature \( T \). Please note that, experimentally, the change in area is measured for the pellet and hence the area thermal coefficient expansion is expressed as

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

[3]

The thermal expansion coefficient, thus estimated from Figure 3, aligns reasonably well with the reported values of pure magnetite. Using the estimated thermal expansion coefficient, the percentage area change due to sintering, \( \delta_{\text{sintering}} \), was isolated from the overall change in area, \( \delta_{\text{overall}} \). Subsequent analysis has been performed after isolating the percentage area change due to sintering alone (\( \delta_{\text{sintering}} \)).

Sintering is a thermally activated process, and hence the degree of sintering is expected to increase with increasing temperature. Figure 4 depicts the rate of sintering as a function time obtained for different sintering temperatures. Here, the rate of sintering increases with increasing temperature during non-isothermal heating due to enhancement in kinetics with increasing temperature. The rate of sintering decreases with time in the isothermal segment as the driving force for sintering progressively decreases with the extent of sintering. The driving force for sintering is the reduction in the surface area of grains in pellet which also results in reduction in pore volume. The rate of sintering is not only function of temperature but also the extent of sintering remaining (or the extent of sintering that has already occurred). Thus, at a constant temperature, as sintering progresses, the driving force available for further sintering reduces and hence the rate of sintering. It should be noted that experiments have also been repeated to ensure reproducibility of the results shown in Figure 4. Interestingly, the time at which the rate of sintering is the maximum seems slightly earlier than the start of isothermal segment. Authors are unable to explain this observation. Possibly this can be attributed to the temperature control system making a change from a constant heating rate to an isothermal segment.

Fig. 3—Change in area with respect to temperature for pellets exposed to different sintering temperatures for estimation of thermal coefficient of expansion for iron ore concentrate.

Fig. 4—Sintering rates for pellets exposed to different sintering temperatures.
B. Sintering Ratio ($\gamma$)

Wynnyckyj and Fahidy\textsuperscript{[36]} had suggested that the sintering of material can be quantified by capturing its shrinkage and proposed a term sintering ratio (sintering extent). The sintering ratio for the pellet can be defined as the ratio of the sintering accomplished to the sintering yet to be accomplished:

$$\gamma = \frac{\text{sintering accomplished}}{\text{sintering yet to be accomplished}} = \frac{V_0 - V}{V - V_{\text{true}}}$$  \[4\]

where $V_{\text{true}}$ is the volume of the pellet if it would have undergone complete sintering with no pores remaining.

The percentage change in area due to sintering, $\delta A$, can be defined in terms of bulk density of the pellet at any time $\rho$, as

$$\delta A = \frac{2}{3} \left( \frac{\rho_0 - \rho}{\rho} \right) \times 100$$

and

$$\delta A_{\text{true}} = \frac{2}{3} \left( \frac{\rho_0 - \rho_{\text{true}}}{\rho_{\text{true}}} \right) \times 100$$  \[5\]

The true density, $\rho_{\text{true}}$, of the solid constituents in the pellet is measured using Helium pycnometer having a standard deviation of 1 pct.

From Eqs. \[4\] and \[5\],

$$\gamma = \frac{-\delta A_{\text{sintering}}}{\delta A_{\text{true}} + \delta A_{\text{sintering}}}$$  \[6\]

This equation relates the sintering ratio to the percentage area change measured.

C. Estimation of Sintering Kinetic Parameters

Wynnyckyj and Fahidy\textsuperscript{[36]} proposed that the isothermal sintering kinetics can be expressed as

$$\gamma = K t^n$$  \[7\]

where $t$ is the isothermal time, $n$ is time exponent and $K$ is reaction constant. It can be noted that the initial volume $V_0$ used in Eq. \[4\] correspond to start time ($t = 0$) when the pellet is in isothermal state. Further, the variation of reaction constant term, $K$, with respect to temperature was expressed using the following equation

$$\ln \left( TK^{1/n} \right) = \ln K' - \frac{Q}{RT}$$  \[8\]

Fig. 5—Sintering ratio for pellets exposed to different sintering temperatures.

Fig. 6—Time exponent $'n'$ for oxidized magnetite pellets sintered at different temperatures.

Let us denote $\gamma^*$ as the sintering ratio at the start of the isothermal section as illustrated in Figure 5. Thus, it is possible to define a time, $t^*$, which corresponds to a time if the pellet had attained a sintering ratio of $\gamma^*$ from the start under isothermal condition.

If so, one can write Eq. \[7\] as

$$\gamma^* = K (t')^n$$

and beyond $t^*$,

$$\gamma = K (t' + t_m)^n$$.

where $t_m$ is the time measured from the start of isothermal section as illustrated in Figure 5.

From the above two equations,
ln \left( \frac{c_t}{c_0} \right) = n \ln \left( \frac{t^* + t_m}{t} \right). \quad [9]

Using the data of sintering ratios on the isothermal segment and Eq. [9], the parameters \( n \) and \( t^* \) were estimated using least square fit for different experiments. With these estimated parameters, Eq. [9] has been plotted for experiments with different sintering temperatures shown in Figure 6. The straight lines indicate that Eq. [7] is excellent in capturing the sintering kinetics. The slope of the straight lines gives the \( 'n' \) value. The values of \( n \) for different experiments are shown in Table III. The mean value of the \( n \) and its standard deviation were found to be 0.2099 and 2.57 pct, respectively.

Further, the values of \( K \) were estimated for sintering temperatures and Eq. [8] was used to estimate the values of \( K^* \) and the activation energy \( Q \). The plot showing the \( 1/T \) vs \( \ln(KT^{1/n}) \) is shown in Figure 7. Computed sintering kinetic parameters, namely, \( n, K^* \) and \( Q \) are shown in Table III.

### Table III. Sintering Kinetic parameters

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Isothermal Sintering Temperature [K (°C)]</th>
<th>( n )</th>
<th>( Q ) (KJ/mol)</th>
<th>( K^* ) (10^13 s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1423 (1150)</td>
<td>0.2403</td>
<td>509</td>
<td>3.8 \times 10^{13}</td>
</tr>
<tr>
<td>P2</td>
<td>1473 (1200)</td>
<td>0.2312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>1523 (1250)</td>
<td>0.1900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>1523 (1250)</td>
<td>0.2279</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>1573 (1300)</td>
<td>0.2632</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>1573 (1300)</td>
<td>0.2216</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>1623 (1350)</td>
<td>0.1934</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D. Sintering Prediction Using Kinetic Parameters

In the actual industrial induration process, sintering occurs under non-isothermal conditions. Variation of sintering ratio, \( \gamma \), with time under isothermal condition described by Eq. [7] is extended to consider non-isothermal conditions using the following methodology.

Let \( \gamma_{t+\Delta t} \) denote the sintering ratios at time \( t \) and \( t + \Delta t \), respectively, and corresponding temperatures be denoted by \( T_t \) and \( T_{t+\Delta t} \). During this time interval \( \Delta t \), let us say that sintering occurs isothermally at \( T_{t+\Delta t} \) from \( \gamma_t \) to \( \gamma_{t+\Delta t} \) (This is equivalent to discretizing the time-temperature plot with small isothermal steps). If so, the sintering during this time interval \( \Delta t \) can be written as

\[
\gamma_{t+\Delta t} = K(T_{t+\Delta t}) \left( \frac{\gamma_t}{K^*(T_t)} \right)^{1/n} + \Delta t \]  \quad [10]

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

The variation of \( \gamma \) can be obtained by knowing the temporal variation of temperature and the correspond-
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 using the sintering kinetic parameters, namely, $n$, $K'$, and $Q$, it is possible to predict the extent of sintering for any non-isothermal profile using Eq. [10].

**IV. CONCLUSIONS**

The sintering kinetics of a single oxidized magnetite pellet has been experimentally investigated by capturing the in situ shrinkage of the pellet kept in a furnace. The shrinkage was captured using an optical dilatometer which unlike the traditional alumina push-rod dilatometer does not interfere with the process. Sintering, characterized through shrinkage, can be quantified using three kinetic parameters, namely activation energy ($Q$) and rate constant ($K'$) and a time exponent ($n$). These kinetic parameters were deduced from shrinkage data under isothermal conditions. For the oxidized magnetite pellets studied in the current work, the activation energy $Q$ was found to be 509 kJ/mol. A methodology was developed to predict the extent of sintering under non-isothermal condition using the above kinetic parameters. These predictions were validated using experimental data. Quantitative description of sintering in iron ore pellets can not only be useful in predicting the state of the pellet during industrial induration process but also help in optimizing the appropriate raw material mix for making pellets.

**ACKNOWLEDGMENTS**

Authors thank the Hjalmar Lundbohm Research Centre (HLRC) for their financial support. We also thank Ola Eriksson, Daniel Marjavaara, Gustaf Magnusson, Anders Dahlén, Axel Stahlstrom, Klaus Weigel, and Kjell-Ove Mickelson of LKAB for their technical support. We also thank Prof. N. B. Ballal and Prof. M. P. Gururajan of Indian Institute of Technology (IIT) Bombay for valuable discussions.

**NOMENCLATURE**

- $\delta_A$ Overall percentage area change at any instant during induration
- $\delta_A^{\text{sintering}}$ Percentage area change due to sintering any instant during induration
- $\delta_A$ Percentage area change at any instant
- $\delta_A^{\text{true}}$ Percentage area change when pellet has no pores
- $\alpha$ Volumetric thermal coefficient of expansion
- $\beta$ Area thermal coefficient of expansion
- $V_0$ Initial volume of a material
- $V$ Volume of material at any temperature
- $V^{\text{true}}$ Volume of the pellet if it would have undergone complete sintering with no pores
- $T_0$ Initial temperature
- $T_*$ Temperature at any instant
- $\gamma$ Sintering ratio of the pellet
- $\gamma^*$ Sintering ratio at the start of the isothermal section
- $\rho$ Bulk density of the pellet at any instant
- $\rho^{\text{true}}$ True density of the pellet
- $\rho_0$ Initial bulk density of pellet
- $t$ Time for sintering reaction
- $t^*$ Time corresponds if the pellet had attained a sintering ratio of $\gamma^*$ from the start under isothermal condition
- $t_m$ Measured time in isothermal section
- $n$ Time exponent
- $k$ Reaction rate constant
- $Q$ Activation energy
- $R$ Universal gas constant
- $T_{t}$ Temperature at time $t$
- $T_{t+\Delta t}$ Temperature at time $t + \Delta t$
- $K(T_{t+\Delta t})$ Rate constant at $t + \Delta t$

**REFERENCES**

Erratum to: Estimation of Sintering Kinetics of Oxidized Magnetite Pellet using Optical Dilatometer

T.K. SANDEEP KUMAR, NEELAKANTAN NURNI VISWANATHAN, HESHAM H. AHMED, CHARLOTTE ANDERSSON, and BO BJÖRKMAN

DOI: 10.1007/s11663-016-0844-1

Erratum to: METALLURGICAL AND MATERIALS TRANSACTIONS B, VOL. 46B, PP. 635–643, 2015, DOI: 10.1007/s11663-014-0273-y

AUTHORS have used a new way for measuring bulk volume based on the image (pixel) analysis named as Light Table Imaging (LTI), and subsequently bulk densities and porosities. Authors lately found that there was a slight error in calibrating the scale (known distance) to pixel measurement and understand the need to communicate the error and subsequent corrections.

After correcting the calibration scale appropriately, the corresponding corrections have been implemented to evaluate the values of bulk volume, bulk density, porosity, sintering ratio and further kinetic parameters for all the pellets used in the study. The corrections have only changes the absolute values and does not affect or changed the understanding, outcome and conclusions of the study. Therefore, it is requested to incorporate the changes – Figures and Table by the corrected ones as mentioned below.

LIST OF CORRECTIONS
1. Page 635, Abstract, Line 16/17: ‘’...and reaction rate constant ($K_c$) are estimated.’’ should be replaced by ‘’...and pre-exponential factor ($K_c$) are estimated.’’
2. Figures which should be replaced with the corresponding ones as shown below:
   i. Page 638, Fig. 2
   ii. Page 639, Fig. 3
   iii. Page 639, Fig. 4
   iv. Page 640, Fig. 5
   v. Page 640, Fig. 6
   vi. Page 641, Fig. 7
   vii. Page 641, Fig. 8
   viii. Page 642, Fig. 9

Fig. 2—Typical shrinkage curve obtained from Optical Dilatometer.

T.K. SANDEEP KUMAR, Doctorate Student, and BO BJÖRKMAN, Chaired Professor, are with the Department of Civil, Environmental and Natural Resources (SBN), Luleå University of Technology (LTU), 97187 Luleå, Sweden. Contact e-mail: kamesh.sandeep@ltu.se NEELAKANTAN NURNI VISWANATHAN, Visiting Professor is with the Department of Civil, Environmental and Natural Resources (SBN), Luleå 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), Luleå University of Technology (LTU), and also with the Central Metallurgical Research & Development Institute (CMRDI), Cairo, Egypt. CHARLOTTE ANDERSSON, Specialist/Senior Researcher, is with the Oxidation Metallurgy, Research & Development, Luossavaara-Kiirunavaara AB (LKAB), Malmberget, 90381 Gällivare, Sweden.

The online version of the original article can be found under doi: 10.1007/s11663-014-0273-y.

METALLURGICAL AND MATERIALS TRANSACTIONS B

Published online: 28 October 2016
Fig. 3—Change in area with respect to temperature for pellets exposed to different sintering temperatures for estimation of thermal coefficient of expansion for iron ore concentrate.

Fig. 4—Sintering rates for pellets exposed to different sintering temperatures.

Fig. 5—Sintering ratio for pellets exposed to different sintering temperatures.

Fig. 6—Time exponent $n$ for oxidized magnetite pellets sintered at different temperatures.
3. Page 641, Table III should be replaced by the corresponding table mentioned below.

4. Page 641, Line 11: “...were found to be 0.2099 and 2.57 pct, respectively” should be replaced by “...were found to be 0.2373 and 1.16 pct, respectively”.

5. Page 642, Conclusions, Line 9: “...and rate constant ($K'$) ...” should be replaced by “...and pre-exponential factor ($K'$)...”.

6. Page 642, Conclusions, Line 13: “...$Q$ was found to be 509 kJ/mol.” should be replaced by “…$Q$ was found to be 464 kJ/mol.”

Table III. Sintering Kinetic Parameters

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Isothermal Sintering Temperature [K (°C)]</th>
<th>$n$</th>
<th>$Q$ [kJ/mol]</th>
<th>$K'$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1423 (1150)</td>
<td>0.2438</td>
<td>464</td>
<td>5.21 x 10$^{13}$</td>
</tr>
<tr>
<td>P2</td>
<td>1473 (1200)</td>
<td>0.2375</td>
<td>464</td>
<td>5.21 x 10$^{13}$</td>
</tr>
<tr>
<td>P3</td>
<td>1523 (1250)</td>
<td>0.2187</td>
<td>464</td>
<td>5.21 x 10$^{13}$</td>
</tr>
<tr>
<td>P4</td>
<td>1573 (1300)</td>
<td>0.2371</td>
<td>464</td>
<td>5.21 x 10$^{13}$</td>
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<tr>
<td>P5</td>
<td>1623 (1350)</td>
<td>0.2406</td>
<td>464</td>
<td>5.21 x 10$^{13}$</td>
</tr>
</tbody>
</table>
Paper II
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 focuses 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.


1. 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 subjected to sintering, and this is further complicated by the heat generated within the pellet from the exothermic oxidation of magnetite, and sintering occurs. Ideally, it is desirable to have sintering after the complete oxidation of magnetite. 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. 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, 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 \(^1\) to \(^13\) 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. \(^1\) 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 \(^1\) to \(^20\) whereas those of iron ore \(^21\) to \(^27\) 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, Wynnyckyj and Fahidy made an early attempt by studying 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.

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. \(^1\) 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 ~9900 cm\(^2\)/cm\(^3\) (Blaine No. = 1930 cm\(^2\)/gm) measured by Brunauer-Emmett-Teller (BET) Surface Area analyzer. The concentrate having Fe\(_2\)O\(_3\) with Al\(_2\)O\(_3\) and 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. \(^1\) 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

<table>
<thead>
<tr>
<th>Concentrate (Wt Pct)</th>
<th>Bentonite (Wt Pct)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>71.06</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.39</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>0.26</td>
</tr>
<tr>
<td>Σ Na(_2)O + K(_2)O</td>
<td>0.078</td>
</tr>
</tbody>
</table>

**METALLURGICAL AND MATERIALS TRANSACTIONS B**
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 × 10⁻⁶ m³/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 infiltration 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.

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

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
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.

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. 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 ($\alpha$) is related to its area thermal coefficient of expansion ($\beta$), and is expressed in
The values of thermal expansion estimated are comparable with that obtained in the literature. 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 ($\gamma$)

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, Wynnyckyj 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.

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

where $V_0$ is the initial volume of the pellet, $V$ is the volume of the pellet at any instant during sintering and $V_{\text{true}}$ 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.

\[ \gamma = \frac{-\delta A_{\text{sintering}}}{\delta A_{\text{true}} + \delta A_{\text{sintering}}} \]  

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 ($\gamma$) with a time exponent ($\alpha$), as expressed in Eq. [5]. The time exponent of the reaction determines the reaction mechanisms which are dominant during sintering of pellet at various stages as it progresses.

\[ \gamma = Ke^{\alpha} \]
where $K$ is the rate constant. Further, this reaction constant term can be related to temperature with an Arrhenius form of expression (Eq. [6]).

$$\ln \left( \frac{T}{K_0} \right) = \ln K' - \frac{Q}{RT}$$  \hspace{1cm} [6]$$

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

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,
\begin{equation}
\ln \left( \frac{\gamma}{\gamma^*} \right) = n \ln \left( \frac{t + t_m}{t^*} \right)
\end{equation}

where \( \gamma^* \) 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 \( \gamma^* \) 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 \( \gamma \), 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 \( (R^2 > 0.975 \text{ and } \sigma < 0.04) \) 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 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

\begin{equation}
n = -4 \times 10^{-4}T + 0.72
\end{equation}

Further, from the variation of sintering ratio, \( \gamma \), with time, \( t \), in the isothermal section the values of sintering rate constant, \( K \), in Eq. [5] for different temperatures is estimated knowing respective \( \gamma^* \), \( t^* \), and \( n \). In order to estimate the activation energy, \( Q \) and the pre-exponential factor, \( K_0 \). \( \ln (KT^{n'}) \) 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 magnetic 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 \( \Delta t \) (discretized time – temperature plot) to generate the profile for sintering ratios as expressed in Eq. [9].

\begin{equation}
\gamma_{t+\Delta t} = K(T_{t+\Delta t}) \left( \frac{\gamma_t}{K(T_{t+\Delta t})} \right)^{1/n} + \Delta t
\end{equation}

where \( \gamma_t \) 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 \( (\frac{\gamma_t}{K(T_{t+\Delta t})})^{1/n} \) is the time that would have taken to achieve sintering ratio of \( \gamma_t \) isothermally at temperature \( T_{t+\Delta t} \).
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 appear 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 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

### Table III. Kinetic Parameters for Sintering of Magnetite Pellets

<table>
<thead>
<tr>
<th>Sintering Temp. [K (°C)]</th>
<th>( n )</th>
<th>( K \times 10^{-3} ) (s(^{-1}))</th>
<th>( t^* ) (s)</th>
<th>Activation Energy (kJ/mole)</th>
<th>Pre-exponential Factor (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173 (900)</td>
<td>0.35</td>
<td>8.2</td>
<td>953.81</td>
<td>( Q_2 = 477 \text{ kJ/mole} )</td>
<td>( K_0^2 = 3.66 \times 10^{14} )</td>
</tr>
<tr>
<td>1223 (950)</td>
<td>0.31</td>
<td>1.6</td>
<td>832.86</td>
<td>[1173 K to 1373 K] (900 °C to 1100 °C)]</td>
<td>[1173 K to 1373 K] (900 °C to 1100 °C)]</td>
</tr>
<tr>
<td>1248 (975)</td>
<td>0.20</td>
<td>6.1</td>
<td>192.20</td>
<td>( Q_3 = 477 \text{ kJ/mole} )</td>
<td>( K_0^3 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1273 (1000)</td>
<td>0.44</td>
<td>1.1</td>
<td>849.93</td>
<td>[1373 K to 1623 K] (1100 °C to 1350 °C)]</td>
<td>[1373 K to 1623 K] (1100 °C to 1350 °C)]</td>
</tr>
<tr>
<td>1298 (1025)</td>
<td>0.25</td>
<td>6.9</td>
<td>242.56</td>
<td>( Q_4 = 477 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1323 (1050)</td>
<td>0.35</td>
<td>3.7</td>
<td>533.74</td>
<td>[1373 K to 1623 K] (1100 °C to 1350 °C)]</td>
<td>[1373 K to 1623 K] (1100 °C to 1350 °C)]</td>
</tr>
<tr>
<td>1373 (1100)</td>
<td>0.33</td>
<td>7.8</td>
<td>412.57</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1423 (1150)</td>
<td>0.30</td>
<td>17.4</td>
<td>367.82</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1473 (1200)</td>
<td>0.25</td>
<td>27.9</td>
<td>351.66</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1523 (1250)</td>
<td>0.22</td>
<td>39.9</td>
<td>474.17</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1573 (1300)</td>
<td>0.20</td>
<td>58.8</td>
<td>471.17</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
<tr>
<td>1623 (1350)</td>
<td>0.15</td>
<td>141.3</td>
<td>217.95</td>
<td>( Q_4 = 148 \text{ kJ/mole} )</td>
<td>( K_0^4 = 3.51 \times 10^{12} )</td>
</tr>
</tbody>
</table>

Fig. 11—Variation of time exponent ‘\( n \)’ for pellets exposed to different sintering temperatures.

Fig. 12—Activation energies and pre-exponential factors for the sintering of magnetite pellets.
Sintering was also observed by Wynnyckyj and Fahidy. As far as activation energy is concerned, Xuebin et al. 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 temperatures 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 with partial pressure of oxygen (P₀₂) and temperature. They found that diffusion of iron in magnetite lattice occurs by two different mechanisms—interstitial mechanism (at lower P₀₂ and higher temperature) and vacancy mechanism (at higher P₀₂ 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 P₀₂ 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 P₀₂ > 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.

Interestingly, Xuebin et al. 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 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.

ACKNOWLEDGMENTS

The authors thank the Hjalmar Lundbohm Research Centre (HLRC) for their financial support. We also thank Ola Eriksson, Daniel Marjavaara, Gustaf Magnusson, Magnus Stafstedt, and Anders Dahlin of LKAB for their technical support. We also thank Prof. S. Sesharaman, an Emeritus professor of Royal Institute of Technology (KTH), Stockholm for valuable discussions.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{t,\text{overall}}$</td>
<td>Overall percentage area change at any instant during induration</td>
</tr>
<tr>
<td>$\delta_{t,\text{sintering}}$</td>
<td>Percentage area change due to sintering at any instant during induration</td>
</tr>
<tr>
<td>$\delta_{t,\text{true}}$</td>
<td>Percentage area change at any instant for pores</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Volumetric thermal coefficient of expansion</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Area thermal coefficient of expansion</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Initial volume of a material</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of material at any temperature</td>
</tr>
<tr>
<td>$V_{\text{true}}$</td>
<td>Volume of the pellet if it would have undergone complete sintering with no pores</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Initial temperature ($t = 0$)</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature at any instant</td>
</tr>
<tr>
<td>$\gamma^*$</td>
<td>Sintering Ratio of the pellet at any instant in the isothermal section</td>
</tr>
<tr>
<td>$\gamma^*$</td>
<td>Sintering ratio at the start of the isothermal section</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Bulk density of the pellet at any instant</td>
</tr>
<tr>
<td>$\rho_{\text{true}}$</td>
<td>True density of the pellet</td>
</tr>
<tr>
<td>$t$</td>
<td>Time for sintering reaction</td>
</tr>
<tr>
<td>$t^*$</td>
<td>Time corresponds if the pellet had attained a sintering ratio of $\gamma^*$</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>Measured time in isothermal section</td>
</tr>
<tr>
<td>$n$</td>
<td>Time exponent</td>
</tr>
<tr>
<td>$K_0$</td>
<td>Pre-exponential factor at low temperatures</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Pre-exponential factor at high temperatures</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>Activation energy at low temperatures</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>Activation energy at high temperatures</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
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<tr>
<td>$T(t)$</td>
<td>Temperature at time $t$</td>
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<tr>
<td>$\gamma(t)$</td>
<td>Sintering ratio at time $t$</td>
</tr>
<tr>
<td>$\gamma(t + \Delta t)$</td>
<td>Sintering ratio at time $t + \Delta t$</td>
</tr>
<tr>
<td>$T(t + \Delta t)$</td>
<td>Temperature at time $t + \Delta t$</td>
</tr>
<tr>
<td>$K(T(t + \Delta t))$</td>
<td>Rate constant at $t + \Delta t$</td>
</tr>
</tbody>
</table>

REFERENCES

Erratum to: 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

DOI: 10.1007/s11663-016-0843-2


AUTHORS have used a new way for measuring bulk volume based on the image (pixel) analysis named as Light Table Imaging (LTI), and subsequently bulk densities and porosities. Authors lately found that there was a slight error in calibrating the scale (known distance) to pixel measurement and understand the need to communicate the error and subsequent corrections.

After correcting the calibration scale appropriately, the corresponding corrections have been implemented to evaluate the values of bulk volume, bulk density, porosity, sintering ratio and further kinetic parameters for all the pellets used in the study. The corrections have only changes the absolute values and does not affected or changed the understanding, outcome and conclusions of the study. Therefore, it is requested to incorporate the changes – Figures and Table by the corrected ones as mentioned below.

LIST OF CORRECTIONS

1. Page 309, Abstract, Line 13/14: “...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)...” should be replaced by “...two activation energies—451 kJ/mole [1173 K to 1523 K (900 °C to 1250 °C)] and 162 kJ/mole [1523 K to 1623 K (1250 °C to 1350 °C)...”

2. Figures which should be replaced with the corresponding ones as shown below:
   i. Page 314, Fig. 8
   ii. Page 315, Fig. 9
   iii. Page 315, Fig. 10
   iv. Page 316, Fig. 11
   v. Page 316, Fig. 12
   vi. Page 317, Fig. 13

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The online version of the original article can be found under doi: 10.1007/s11663-015-0505-9.

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Published online: 26 October 2016

Fig. 8—Sintering ratio for magnetite pellets during sintering at different temperatures.
3. Page 315, Line 32: “The value of \( n \) varies from 0.45 to 0.15 in the range…” should be replaced by “The value of \( n \) varies from 0.45 to 0.19 in the range…”.

4. Page 315, Equation [8] should be replaced by the following equation

\[ n = -3.63 \times 10^{-4}T + 0.813 \]

5. Page 316, Table III should be replaced by the corresponding table mentioned here.

6. Page 318, Conclusions, Line 10:

“…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

\[
Q_1 = 162 \text{ kJ/mole} \\
Q_2 = 451 \text{ kJ/mole}
\]

\[
K_1 = 5.57 \times 10^4 \\
K_2 = 3.20 \times 10^{14}
\]

---

**Table III. Kinetic Parameters for Sintering of Magnetite Pellets**

<table>
<thead>
<tr>
<th>Sintering Temp. [K (°C)]</th>
<th>( n )</th>
<th>( K ) ( \times 10^{-3} ) (s (^{-1} ))</th>
<th>( t^* ) (s)</th>
<th>Activation Energy (kJ/mole)</th>
<th>Pre-exponential Factor (K/s)</th>
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</thead>
<tbody>
<tr>
<td>1173 (900)</td>
<td>0.38</td>
<td>0.8</td>
<td>703.13</td>
<td>( Q_1 = 451 \text{ kJ/mole} )</td>
<td>( K_1 = 5.57 \times 10^4 )</td>
</tr>
<tr>
<td>1223 (950)</td>
<td>0.31</td>
<td>2.5</td>
<td>837.99</td>
<td>( (1173 \text{ K} \text{ – } 1523 \text{ K}) )</td>
<td>( (900 \text{ °C} \text{ – } 1250 \text{ °C}) )</td>
</tr>
<tr>
<td>1248 (975)</td>
<td>0.28</td>
<td>4.2</td>
<td>143.59</td>
<td>( (900 \text{ °C} \text{ – } 1250 \text{ °C}) )</td>
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</tr>
<tr>
<td>1273 (1000)</td>
<td>0.45</td>
<td>1.7</td>
<td>866.39</td>
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<tr>
<td>1298 (1025)</td>
<td>0.26</td>
<td>10.6</td>
<td>246.81</td>
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<tr>
<td>1323 (1050)</td>
<td>0.36</td>
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<tr>
<td>1373 (1100)</td>
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<td>10.6</td>
<td>428.56</td>
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<tr>
<td>1423 (1150)</td>
<td>0.32</td>
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<td>387.71</td>
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<tr>
<td>1473 (1200)</td>
<td>0.28</td>
<td>42.3</td>
<td>315.34</td>
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<tr>
<td>1523 (1250)</td>
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<td>73.1</td>
<td>507.45</td>
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<tr>
<td>1573 (1300)</td>
<td>0.25</td>
<td>78.0</td>
<td>510.25</td>
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<tr>
<td>1623 (1350)</td>
<td>0.19</td>
<td>206.5</td>
<td>234.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

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477 kJ/mol and 148 kJ/mol, 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)].

...should be replaced by

"...the value of \( n \) varies from 0.45 to 0.19 with the increase in temperature. The two activation energy values estimated for the sintering of magnetite pellets are 451 kJ/mol and 162 kJ/mol, respectively, at lower temperatures [1173 K to 1523 K (900 °C to 1250 °C)] and higher temperatures [1523 K to 1623 K (1250 °C to 1350 °C)]."

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

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).
Paper III
Establishing a Novel Methodology to Correlate the Macroscopic and Microscopic Degree of Sintering in Magnetite Pellets during Induration

Telkicherla Kamesh Sandeep Kumar,* Martin Simonsson, Nurni Neelakanta Viswanathan, Hesham Ahmed, Charlotte Andersson, Abdel-Hady A. El-Geassy, and Bo Björkman

The quality of product pellets is a result of the physico-chemical phenomena involved in the induration process. Sintering is the primary phenomenon, and its degree or extent contributes substantially to the evolution of the metallurgical and mechanical properties of a pellet. During the induration of magnetite pellets, sintering proceeds through the oxidized and non-oxidized magnetite phases. Sintering of these phases has been previously studied on a single pellet at the macroscopic scale using an optical dilatometer. A deeper understanding requires corroboration of these studies through characterization at the microscopic scale. In the present work, the observations recorded at the microscopic scale are quantified using image processing techniques to correlate them to the macroscopic measurements. Distance transformations, which is an image processing principle, is adapted in a novel way to digitize the microstructures and to determine the degree of sintering in a pellet quantitatively. This methodology has potential applications as a generic tool to follow the sintering phenomenon and process kinetics at any stage during induration.

1. Introduction

Pelletization is a vital process in the mineral and metallurgical industries to minimize dust and particulate emissions into the atmosphere and achieve compliance with regulations enacted by various international environmental regulatory agencies.[1–4] During pelletization, ultra-fine-sized ore is agglomerated and indurated to make the process sustainable considering the scarcity of high-grade (size and chemistry) mineral resources (ores).[5–9]

In Sweden, there are rich deposits of iron ore in the form of magnetite. Luossavaara-Kirunavaara Aktiebolag (LKAB) is one of the premier pellet producers in the world and operates in Malmberget and Kiruna. During pelletization, the mine ore is crushed to a fine size (<3 mm), magnetically separated from the gangue and ground to an ultra-fine size (<150 μm). The finely ground ore is then balled into spherical pellets (10–12.5 mm diameter) with the addition of optimum amounts of moisture and additives such as binder and flux. Thereafter, the green pellets are fired (heat hardened) under an oxidizing atmosphere inside an induration furnace (straight grate or rotary kiln) to temperatures of approximately 1573 K. Afterward, the fired pellets are cooled, stored, and transported to customers for further processing.[10–12]

A magnetite pellet undergoes oxidation initially and sintering at relatively higher temperatures (>1073 K). Sintering is responsible for imparting the pellets with adequate mechanical strength and metallurgical properties.[13–15] Therefore, the sintering phenomenon must be investigated and understood to enable the design of the optimum thermal profile for consistently producing good-quality pellets. Because sintering is preceded by oxidation, a magnetite pellet often transforms into oxidized magnetite (hematite), remains as non-oxidized magnetite (magnetite) or transforms into a mix of the two prior to the initiation of sintering. The difference in sinterability of both of these phases at high temperatures results in different sintering behavior. To account for these factors, researchers have investigated sintering macroscopically using optical dilatometry for oxidized and non-oxidized magnetite pellets.[11,13,14] Isothermal sintering studies have been performed to estimate the kinetic parameters and predict the respective sintering behavior. Establishing the physical significance of the findings on a macroscopic scale requires their substantiation on the microscopic scale and the development of a correlation.

The microstructural features of pellets often provide insights into their corresponding metallurgical and mechanical properties. Most of these properties, including the cold crushing strength, high-temperature strength, reducibility, and extent of...
reaction are primarily the result of the sintering degree (bonding), phase content and distribution, porosity, and the pore size distribution in the pellets.\cite{7–12,15–23} Digitization of microstructural images enables the quantification of many of these features and further correlates the pellet properties empirically with the aid of reactor scale and statistical models.\cite{20,24–32} Models and software packages have been developed to determine features such as phase quantification and pore size distribution from microstructures, whereas none have been developed to determine the sintering degree. Therefore, the objective of this study is to estimate the sintering degree quantitatively by inspecting the optical microstructures of pellets sintered at different isothermal temperatures and to correlate these results with the macroscopically observed features. In the future, the goal is to relate the sintering degree to the other aforementioned features to evaluate the pellet quality with the aid of models developed using extensive experimentation.

According to the two-particle sintering theory, the sintering degree estimated from the microstructures can be defined as the ratio of neck thickness ($X$) to the interparticle distance ($D$) between two spherical particles, as mentioned in Equation \ref{eq:1}:

$$\text{Sintering Degree} (\gamma) = \frac{\text{Neck thickness} (X)}{\text{Interparticle distance} (D)} \times \frac{1}{\text{Perimeter}}$$  \hspace{1cm} (1)

When the two particles adhere or begin to sinter with each other, the neck thickness $X$ increases and the interparticle distance $D$ between them decreases. This behavior results in an increase of the $X/D$ ratio as the sintering between particles proceeds by adhesion, neck formation, and bond formation, as shown schematically in Figure 1. This behavior decrease in perimeter as sintering progresses forms the basis for the estimation of the sintering degree $\gamma$ from the microstructures. Distance transform, which is an image processing principle, has been used in a novel way with pellet microstructures for this purpose.\cite{150} The distance transform is an operator that transforms the binary input image such that the gray level intensities of points inside the foreground regions are transformed to show the distance to the closest boundary from each point, as shown in Figure 2.\cite{150}

Distance transform applied to pellet microstructures computes the perimeter of the sintered particles at each pixel distance from the edge of a particle inwards. This approach provides the shortest pixel distance to the edge of a particle as the measure of the sintering extent, which measures the size of the sintered particles. Subsequently, a histogram is generated that provides the pellet particle size distribution. If the number of sintered (larger) particles in the pellet is greater than what is observed in a green pellet, the extent of sintering is greater, and vice-versa.

Figure 1. Schematic of the process of the two-particle sintering theory showing the increasing $X/D$ ratio and decreasing perimeter.

Figure 2. Schematic of the distance transformation of a binary image outlining the perimeter at each pixel layer (red = 1 pixel and blue = 2 pixels distance from surface).\cite{150}
2. Characterization Methods

2.1. Raw Material

The particle size distribution of the concentrate used in this study to prepare the pellets was targeted to have fineness of 65 wt%; it was passed through 45 μm screens and exhibited a specific surface area of \( \frac{9900 \text{ cm}^2}{\text{g}} \) (Blaine No. = 1930 cm\(^2\) g\(^{-1}\)) when measured using a Brunauer–Emmett–Teller (BET) surface area analyzer.

2.2. Macroscopic Analysis—Optical Dilatometer

2.2.1. Measurement of Shrinkage and Sintering Degree of Pellet

Sintering of the pellets or porous compacts is accompanied by volumetric shrinkage when the sintering is carried out at high temperatures. Optical dilatometry, which is based on the principle of light optics, was used for this purpose, as described in previous studies.\(^{[13,14]}\) In optical dilatometry, shadow images are captured continuously and subsequently used to measure the shrinkage of the pellet and the sintering degree for a given thermal profile.

2.3. Microscopic Analysis—Optical Microstructures

2.3.1. Sample Preparation

A total of 16 samples were investigated in the current study. The green pellet was dried in an oven at 423 K overnight prior to being mounted and polished. The sintering behavior of oxidized and non-oxidized magnetite pellets exposed to the different thermal profiles mentioned in Table 1 were studied previously at the macroscopic scale.\(^{[13,14]}\) Thereafter, the same pellets were investigated microscopically in this study. The pellets were cut into half by using a diamond saw and then cold mounted in epoxy, vacuum impregnated, and polished to a fineness of 1 μm with diamond paste to attain a flat reflecting pellet surface for microscopic examination.

2.3.2. Acquisition and Processing of the Microstructural Images

The microstructure of the pellet across the entire cross section area was acquired for further digitization and quantification. An optical microscope (Zeiss Imager M2m, Germany) equipped with a mechanized movable stage and image analysis software from AxioVision was used for this purpose.\(^{[37]}\) The epoxy-mounted polished pellet sample was placed at the center of the microscope stage. The stage was then programmed to move over a desired scan area (5 × 5 μm\(^2\)) for each image at a magnification of 1000×.

![Figure 3. Optical microstructure of the pellet (shown in its entirety) generated by stitching several images together using the mosaic feature.](image-url)
of 200 × 200 using the MosaiX module in the AxioVision software. At a magnification of 200× for one pellet with a diameter of 10 mm, more than 1000 grayscale images with a size of 1388 × 1040 pixels were acquired. The images were acquired with a 10% overlap to allow efficient stitching. The spatial resolution determined using a calibration scale was 0.32 μm per pixel. Automatic focusing at each stage position was used to ensure good focus on the target over the cross-sectional area.

Figure 4. a) Optical microstructure of a pellet at the gray level processed to create the b) binary mask (one (1) = hematite or magnetite phase and zero (0) = pores) and c) the distance transformed image (pixel layer-wise color on the perimeter, moving inwards from the edge of the particles).

Figure 5. Optical microstructures for oxidized magnetite (OM) and non-oxidized magnetite (M) pellets with respect to a green pellet over the temperature range 1423–1623 K.
2.3.2.1. Illumination Correction and Stitching
Because the illumination in microscopes is uneven (the intensity is slightly greater at the center), the images must be corrected to avoid a checkered appearance when stitched together. The illumination level was estimated from more than 15 images corresponding to the epoxy portion via median filtering. A median for all the filtered images was then calculated and used to normalize the entire image data set. Thereafter, the images were filtered and processed for illumination correction and then stitched together, as shown in Figure 3.

2.3.2.2. Pixel Classification
The images were classified and segmented using the Ilastik,[39] which uses a filter bank to process the images. The filters were designed to enhance edges, extract texture, and color/intensity information. The filters extract information about each pixel and its surroundings. This information is then used by the classifier to classify the pixels into different groups: hematite, magnetite, pores, gangue, and epoxy. The segmentation was refined by selecting more pixels so that the classifier could train until satisfactory segmentation was achieved. The training was performed on a subset of images in the data set prior to the classifier being applied to the entire data set. The output of the classifier was an image in which each pixel was labeled with a number corresponding to one of the defined classes.

2.3.2.3. Binary Mask and Distance Transform
From the output of the classifier, binary masks were created for each class by assigning pixels with the selected class to one (1) and all other pixels to zero (0). This procedure was carried out for the two primary classes to create binary masks for areas corresponding to hematite and magnetite, respectively. Because the pellet was surrounded by epoxy in all the samples, the epoxy class was used to delineate the area corresponding to the pellet and to create a binary mask of the pellet. A hole-filling algorithm was used to create a binary mask of the solid pellet (Figure 4a), where the pores were removed from the interior of the pellet, as shown in Figure 4b.[40]

The distance transform for the binary mask of the pellet was computed, as shown in Figure 4c; a histogram of the distance map gives the number of pixels for every pixel distance from the edge of the pellet. Because the spherical shape of the pellet results in more pixels with a shorter distance to the edge of the pellet, the ratio of each class for every distance was calculated by normalizing to the histogram from the unmasked distance map.

2.3.3. Evaluation of the Sintering Degree from Optically Recorded Microstructures
When the pellet was exposed to a thermal profile, the smaller particles coalesced together to form larger particles via bond formation. The histogram constructed from the distance map gives the number of pixels for every pixel distance from the edge of the pellet. Because the spherical shape of the pellet results in more pixels with a shorter distance to the edge of the pellet, the ratio of each class for every distance was calculated by normalizing to the histogram from the unmasked distance map.

2.3.3.1. Sintering Degree
In thermally treated pellets to that of the green pellet is termed the sintering degree, as defined in Equation (2):

$$\text{Sintering Degree} (\gamma) = \frac{\text{Cum. fraction of sintered particles in thermally treated pellet}}{\text{Cum. fraction of particles in green pellet}} \times 100$$

(2)

3. Results and Discussion
3.1. Optical Microstructures
Optical microstructures of the entire pellet (mosaic optical microstructures) were acquired and inspected for all the pellets considered in the study. For brevity and clarity, a thin strip of the microstructure from each of the mosaic optical images is presented in Figure 5.

For both oxidized and non-oxidized magnetite pellets, an increase was observed in the extent of sintering with temperature, with the green pellet as the reference sample. This result was expected and consistent with the theoretical understanding of the sintering phenomenon.[1,34,41] This result, therefore, substantiates the approach adapted in this study to process the mosaic optical microstructures to estimate the sintering degree quantitatively.
3.2. Microscopic Particle Size Distribution

The histograms from the distance transform performed on the mosaic optical microstructures for the oxidized and non-oxidized magnetite sintered pellets at different temperatures, along with that from the green pellet, are shown in Figure 6. The percentages shown in Figure 6 represent number fractions, which differ substantially from volume fractions, which were obtained from a laser particle size analyzer. The particles in the size range from 0.32 to 4.85 μm constitute approximately 80% (the number fraction that considers particle sizes larger than 0.32 μm) in the pellets and are expected to contribute significantly to the overall sintering degree. In the later part of the discussion, this contribution becomes evident from the results.

The histograms from the distance transform performed on the mosaic optical microstructures for the oxidized and non-oxidized magnetite sintered pellets at different temperatures, along with that from the green pellet, are shown in Figure 6. The percentages shown in Figure 6 represent number fractions, which differ substantially from volume fractions, which were obtained from a laser particle size analyzer. The particles in the size range from 0.32 to 4.85 μm constitute approximately 80% (the number fraction that considers particle sizes larger than 0.32 μm) in the pellets and are expected to contribute significantly to the overall sintering degree. In the later part of the discussion, this contribution becomes evident from the results.

Figure 6 shows that the green pellet had a higher fraction of small particles, whereas the fraction of smaller particles decreased and the fraction of larger particles increased as the sintering temperature was increased from 1173/1423 to 1623 K. The approximate particle size was identified, where the variations in the fraction of particles between the green pellet and all of the sintered pellets was minimized. A particle size of 0.97 μm (3-pixel distance) was identified in this study and was considered a pivot between sintered and non-sintered particles. This result was consistent for both oxidized and non-oxidized magnetite in the sintered pellets across the range of investigated temperatures. Therefore, particles smaller than 0.97 μm were assumed to participate in the sintering and to agglomerate to form strongly bonded larger particles in the pellet. However, particles larger than 4.85 μm (15-pixel distance) constituted only approximately 20% of the particles in the pellets and had a smaller surface area over which sintering could occur. This smaller surface area resulted in their contribution to sintering bond formation being insignificant compared with that of smaller particles (<4.85 μm). Thus, in this study, the size of the particles in the pellets after sintering varied in the range from 0.97 to 4.85 μm.

3.3. Microscopic Sintering Degree

From the above considerations, Equation 2 was rearranged to estimate the sintering degree by evaluating the relative increase in the number of particles in the size range from 0.97 to 4.85 μm in the sintered pellets with respect to the corresponding number in the green pellet, as mentioned in Equation 3:

\[
\text{Sintering Degree}(\gamma) = \left( \frac{\text{Cum. fraction of particles between 0.97-4.85} \mu\text{m}}{\text{Cum. fraction of particles} < 0.97 \mu\text{m}} \right) \times 100. \tag{3}
\]

Figure 6 shows that the green pellet had a higher fraction of small particles, whereas the fraction of smaller particles decreased and the fraction of larger particles increased as the sintering temperature was increased from 1173/1423 to 1623 K. The approximate particle size was identified, where the variations in the fraction of particles between the green pellet and all of the sintered pellets was minimized. A particle size of 0.97 μm (3-pixel distance) was identified in this study and was considered a pivot between sintered and non-sintered particles. This result was consistent for both oxidized and non-oxidized magnetite in the sintered pellets across the range of investigated temperatures. Therefore, particles smaller than 0.97 μm were assumed to participate in the sintering and to agglomerate to form strongly bonded larger particles in the pellet. However, particles larger than 4.85 μm (15-pixel distance) constituted only approximately 20% of the particles in the pellets and had a smaller surface area over which sintering could occur. This smaller surface area resulted in their contribution to sintering bond formation being insignificant compared with that of smaller particles (<4.85 μm). Thus, in this study, the size of the particles in the pellets after sintering varied in the range from 0.97 to 4.85 μm.

The microscopically estimated sintering degree from Equation 3 was compared with that estimated by optical dilatometry, as detailed in Table 2. This comparison yields a multiplication factor (MF), that is, specific to the pellet type. The average MF for oxidized magnetite and non-oxidized magnetite pellets was 2.2 and 3, respectively. That is, MF correlates the sintering degree estimated at two scales: microscopically over the cross-sectional area of a pellet and macroscopically from the volumetric proportions of the pellet. It is to be noted that MF is specific to the material and should be evaluated by macro- and microscopic sintering investigations for a particular material.

Incorporating the respective MF in Equation 3, the microscopic sintering degrees for both pellet groups at different isothermal sintering temperatures were compared with the data from the optical dilatometer, as shown in Figure 7. The profiles of sintering progress with temperature were in fair agreement for both oxidized and non-oxidized pellets. However, a slight

<table>
<thead>
<tr>
<th>Pellet</th>
<th>Isothermal temp (K)</th>
<th>Sintering degree ((\gamma)), %</th>
<th>Sintering degree ((\gamma)), %</th>
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<td></td>
<td>Optical dilatometer</td>
<td>Optical microscopy</td>
<td>Pellet</td>
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</tr>
<tr>
<td></td>
<td>MF = 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-oxidized magnetite</td>
<td>1423</td>
<td>12.74</td>
<td>6.81</td>
</tr>
<tr>
<td></td>
<td>1223</td>
<td>6.41</td>
<td>4.63</td>
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<tr>
<td></td>
<td>1473</td>
<td>33.19</td>
<td>24.17</td>
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<td></td>
<td>1523</td>
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<td></td>
<td>1623</td>
<td>33.19</td>
<td>24.17</td>
</tr>
<tr>
<td></td>
<td>MF = 3.0</td>
<td></td>
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</table>
scatter was observed in the values estimated by microstructural image quantification for non-oxidized magnetite pellets at lower temperatures (1173–1373 K); this scatter may be due to limitations imposed by the resolution of the smaller grains in the optical microstructures of the pellets exposed to such lower sintering temperatures.

This methodology of quantifying microstructural images to estimate sintering degree is a step toward understanding and monitoring the sintering behavior more comprehensively in a semi-automated manner. This methodology can further be utilized to determine the process kinetics parameters using the isothermal power law and the Arrhenius equation, as described in previous studies [13,14]. Because sintering is the last stage during the induration process, it widely determines the final properties of the pellet. Notably, the pixel classification module has also improved the efficiency of phase classification and its distribution [35]. Therefore, quantitative estimation of sintering behavior and process kinetics in conjunction with the phase classification and pore size distribution might be further helpful in correlating pellet properties. After the methodology is further fine-tuned and validated over several types of pellets, the development of an online module in future can be planned to evaluate pellet quality during induration. This approach can serve as an additional tool for optimizing the process and operational parameters depending on the desired pellet quality.

4. Conclusions
A methodology to establish a correlation between the macroscopic and microscopic features present during the sintering phenomena in pellets (porous powder compacts). In this context, two phases occurring during magnetite pellet induration, oxidized and non-oxidized magnetite, were characterized independently for the sintering degree at both the macroscopic and microscopic scales. Optical dilatometry was used for the macroscopic measurements, and the microscopic measurements were performed by quantifying the optical microstructures using advanced image analysis modules. The distance transform principle was used in a novel way on the mosaic optical microstructures taken from the sintered pellets. As the sintering temperature was increased, the fraction of smaller particles decreased and the fraction of larger particles increased. The pivotal particle size was found to be <0.97 μm in this study. The sintering degree was estimated from the resulting histogram of the particle size distribution. A semi-empirical correlation between the macroscopic and microscopic sintering degree was derived. The multiplication factor (MF) for the oxidized and non-oxidized magnetite pellets considered in the current study was 2.2 and 3, respectively. The microscopic sintering degree of the respective pellets and the trends with temperature were consistent with those obtained from macroscopic investigations. This enabled tracking of the sintering profile of the pellets and the process kinetics at any stage during induration. In the future, this method could be further extended to correlate the pellet quality (mechanical and metallurgical properties) and develop an online tool to assist in optimizing the process and operational parameters.

Acknowledgements
The authors would like to thank the Hjalmar Lundbohm Research Centre (HLRC) for their financial support and LKAB, Malmberget, Sweden for providing access to their laboratory facilities. The authors would also like to thank Axel Stahlstrom (LKAB) for support in acquiring the microstructures and to Lars-Olof Nordin and Staffan Hedvall of LKAB Metlab, Lulea, Sweden for sample preparation.

Keywords
Distance Transform, Induration, Optical Microstructures, Oxidized and Non-oxidized Magnetite Pellets, Sintering Degree

Received: August 25, 2017
Revised: October 18, 2017
Published online:

Paper IV
Investigating the Oxidation Kinetics of Magnetite on Particle Scale

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Abstract

Induration of magnetite pellet is a complex physico-chemical process involving oxidation, sintering and the heat transfer phenomena. These phenomena occur simultaneously and influence each other during induration process. Depending on the thermal and gas composition profile the pellet experiences in an induration reactor, these phenomena could result in the formation of pellets with the duplex structure having a magnetite core and an oxidized magnetite (hematite) outer shell. Due to differing shrinkage characteristics of these two primary phases, cracks develop at the hematite-magnetite interface affecting the quality of the pellets. Therefore, it is necessary to understand the oxidation and sintering phenomena during induration of magnetite pellets. Subsequent to the sintering studies on magnetite pellets, oxidation kinetics of magnetite pellets have been studied in two parts, i.e. at pellet scale as well as at the particle scale are in focus, and the findings of the latter are being presented here. The rate of oxidation of magnetite concentrate is dependent primarily on factors, namely, temperature, the oxygen content in the oxidizing gas and the particle size. These factors are investigated in the current study.

Isothermal oxidation experiments were performed in the Thermo Gravimetric Analyzer (TGA) by inserting the powder sample directly into the isothermal zone at the set oxygen levels. It was found that magnetite concentrate oxidation comprises of two distinct stages, a primary stage with high rates followed by a secondary stage where rates are drastically lowered. The isothermal oxidation behavior was analyzed by Shrinking Core and Avrami Kinetic Models. For the present experimental data, the latter is found to fit better. The partially oxidized particles have also been examined microstructurally, which supplements the experimental as well as model results. Further, the Avrami Kinetic Model for isothermal oxidation is extended to non-isothermal profile using superposition principle and validated using results from non-isothermal experiments.

Key Words

Isothermal Oxidation, Magnetite Concentrate, Thermo Gravimetric Analysis (TGA), Shrinking Core Mechanism Model, Avrami Kinetic Model
1. Introduction

Pelletization of iron ore fines is one of the widely practiced agglomeration technique in the iron and steel making since it enables the use of a very fine concentrate. Iron ore pellets offer several advantages over other ferrous burdens in terms of strength and reducibility along with the uniformity in shape (spherical), chemistry and porosity. Magnetite pelletization provides an added benefit in terms of energy owing to exothermic nature of its oxidation to hematite \(^1\). Magnetite ore excavated from the run-off mines is crushed, beneficiated and ground into fines to a fine concentrate. The concentrate is further balled into green pellets with the addition of moisture and additives such as flux and binder. Thereafter, the green pellets are fired in the induration furnace to impart sufficient strength and attain the desired properties. During induration, the green pellets laid as packed bed undergoes updraft and downdraft drying (RT – 523 K (250°C)) followed by oxidation (573 – 1023 K (300 – 750°C)) and finally sintering (> 1273 K (1000°C))\(^2\), while the hot gases are allowed to flow in the counter-current direction across the furnace for efficient heat transfer.

In order to achieve and enhance the stability in the production of homogeneous and good quality pellets, developing a model that can predict the optimum thermal and gaseous profile for pellets during induration could be fruitful. Therefore, it becomes necessary to understand and estimate the kinetics of the phenomena involved in induration of magnetite pellets. The methodology adopted is to investigate each of the phenomena (oxidation, sintering and heat transfer) on single pellet in isolation, and subsequently integrate together to develop the overall induration model. Sintering models on single pellet scale have already been developed on the basis of their kinetics and demonstrated in the previous studies \(^3,4\). Further, the oxidation kinetic model for magnetite pellet is developed in two parts. In this study, it is intended to investigate the oxidation phenomenon of magnetite concentrate from LKAB’s mine in Malmberget, Sweden on particle scale, estimating their oxidation kinetics and determine the responsible mechanisms. While, the kinetics estimated in this study will help in establishing the oxidation behavior of magnetite at pellet scale, which will be communicated in future.

From the early 1950’s, several researchers have studied the oxidation of magnetite pellets investigating the effect of different sources of concentrate, pellet and particle size distribution with respect to various thermal atmospheres \(^2,5-12\). There have been a lot of experimental studies to capture the oxidation behavior of magnetite on pellet scale, though there are very few being done on particle scale to understand their behavior, estimate their kinetics to develop and validate the model \(^2,5-7,9,13-15\). Oxidation of magnetite concentrate can be simulated to non-catalytic heterogeneous gas-solid reactions. Several models have been proposed to follow the gas-solid reaction sequence which provides the insight into the dominant mechanism in the range of variables studied \(^12,13,16-20\).

One of the gas-solid reaction models, the Shrinking Core Model (SCM) postulates that the oxidation of magnetite concentrate proceeds topo-chemically from the surface towards the center of the particle under the isothermal atmosphere, as mentioned in Equation 1\(^{21}\). It postulates that the mass transfer of the oxidizing gas from bulk to the surface of the particle is rate determining initially. Whereas, once oxygen gas reaches the particle surface, the interfacial
chemical reaction of oxidation of magnetite to hematite becomes dominant with the release of exothermic energy. Thereafter, the oxygen diffuses into the particle along the grain boundaries by diffusion through the hematite product layer due to concentration gradient and proceeds concentrically toward the center of the particle. This results in higher degree or rate of oxidation at the beginning and attains plateau at the later stage.

\[
\frac{r}{3k_m} f + \frac{r}{k_B} \left[ 1 - (1 - f)^{\frac{3}{2}} \right] + \frac{r^2}{6k_g} \left[ 3 - 2f - 3(1 - f)^{\frac{3}{2}} \right] = \frac{CM}{\rho_B} \tau \tag{1}
\]

where, \( f \) is the fraction of conversion for concentrate comprising of particles with an average radii \( r \) for isothermal time \( t \), while \( k_m, k_B \) and \( k_g \) are rate constant for mass transfer of gas, chemical reaction at the interface and diffusivity, respectively. \( M \) and \( \rho_B \) are molar mass and density of the reactant, respectively, whereas \( C \) is oxygen concentration in the reacting gas.

Forsmo \(^{(1)}\) studied the oxidation and sintering phenomena for magnetite pellets prepared from varying magnetite concentrate fineness to understand the mechanisms and optimize the particle size distribution or fineness desired to achieve good quality product pellets. Thereafter, Cho investigated the isothermal oxidation kinetics of magnetite and developed the pellet – particle model \(^{(22)}\). On the other hand, Monsen \textit{et. al} \(^{(15)}\) investigated the kinetics of magnetite oxidation at particle scale in the narrow size fraction for concentrate from different mine source. They also hypothesized that oxidation of magnetite particles proceeds in a topo-chemical manner with the growth of hematite product layer. Though, it was observed that needle-like structure of hematite grew ahead of the reaction front suspecting that the reaction might be proceeding by some other mechanisms. Further, Monazam \textit{et. al} \(^{(23)}\) examined the oxidation of secondary magnetite (i.e. reduced hematite) particles during Chemical Looping Combustion to understand the reaction mechanisms. They found that the oxidation of magnetite particles follows a two-step kinetics phenomenon, which can be described satisfactorily by Avrami Kinetic Model (AKM). AKM describes the kinetics of isothermal phase transformation from one to another, represented by Equation 2. The phase transformation kinetics often follow the sigmoidal (S-shaped) profile with initial slow rates owing to the formation of a sufficient number of nuclei (nucleation), thereafter increases at the rapid rate as nuclei grow into particles (growth) and cease slowly while approaching the complete transformation \(^{(24,25)}\).

\[
f = (1 - e^{-at^n}) \tag{2}
\]

where, \( f \) is conversion/transformation achieved in isothermal \( t \), while coefficients of AKM – \( a \) is the rate constant and \( n \) is the time exponent which provides an insight about the type of nucleation and growth mechanism.
In this study, the isothermal oxidation mechanisms for LKAB’s magnetite concentrate has been investigated experimentally to estimate the kinetic parameters. Isothermal experiments have been performed considering three main parameters as variables, namely, temperature (773 – 1073 K (500 – 800°C)), the partial pressure of O₂ in oxidizing gas (0.05 – 0.21 atm) and average particle size (45.5 – 68.5 μm) of concentrate. Thereafter, the results have been analyzed with the aforementioned two kinetic models – SCM and AKM and compared with the experimental observations to identify the suitable oxidation mechanisms. Further, the non-isothermal behavior is validated by performing non-isothermal experiments.

Isothermal TGA studies can primarily be conducted in two ways: 1) By allowing the sample to reach the isothermal temperature in an inert gas atmosphere subsequently switching the gas from inert to the reactive one (7,9,22) and 2) by inserting the sample in a short duration into the reactor zone kept at desired temperature and gas composition (2). Both these methods have associated disadvantages in terms of initial transients. In the former one, depending on the reactor volume and gas flow rates, it would take some time for the gas composition to reach a stable value. In the latter case, depending on the thermal capacity of the crucible and the sample, it would take some time before the crucible-sample assembly reached desired steady temperature. Most experiments reported in the literature have adopted the former one. In this study, latter has been chosen.

2. Methods and Materials

2.1 Raw Materials

The source of magnetite chosen is the concentrate from LKAB’s mine in Malmberget, Sweden. The concentrate is collected carefully by coning and quartering and contains Fe₂O₃ > 95% with Al₂O₃ and SiO₂ < 0.6%. The concentrate is wet-sieved into three narrow size fractions, 38 to 53 μm (mesh #400), 53 to 63 μm (mesh #270) and 63 to 74 μm (mesh #230) with the average particle diameter ($d_{pa}$) of 45.5 μm, 58 μm, and 68.5 μm, respectively. This enabled to capture the effect of particle size on the inherent oxidation behavior. The sieved concentrates are collected and dried in an oven at 423 K (150°C) overnight. Thereafter, in order to ensure the efficiency of sieving, the sieved particles are further analyzed by Laser-based method (CILAS) for particle size distribution.

2.2 Oxidation Experiments

Isothermal oxidation of magnetite particles is studied with the help of Thermo Gravimetric Analyzer (TGA) (Setaram 92). The TGA consists of a platinum crucible suspended from the weighing balance at the top and lowered into the graphite tube furnace with help of an elevator, as shown in Figure 1.
About 27 mg of narrow size fraction particles (d_p) is poured in the platinum crucible (8 mm in diameter and 5 mm in depth) forming a shallow layer of approximately 2 mm. This is to maintain the resistance due to gas diffusion negligible. S-type thermocouple was placed beneath the sample to measure the temperature. Different proportions (5 – 21%) of O2 in N2 has been used as the oxidizing gas, mixed with the help of a digital gas mixer. The oxidizing gas is allowed to flow from bottom to top of the furnace at the rate of 200 ml/min. This flow rate has been optimized by performing starvation tests. The thermal excursion designed for each of the experiments comprises of heating the furnace up to the isothermal temperature at the rate of 20 K/min, held at isothermal for 60 min followed by cooling at the rate of 20 K/min under the desired oxidizing atmosphere. Once the gas atmosphere has been established and isothermal temperature is reached, the sample is lowered into the furnace. Isothermal oxidation experiments are conducted in the range of temperature, p_O2, and size fraction mentioned in Table 1. Background correction test have also been done for each experiment in TGA by using the empty platinum crucible by following respective thermal and gas profile. The weight gain is continuously captured at every one second by the data logger and corrected by background tests, which are then used for further analysis. Non-isothermal oxidation experiments have been conducted at the heating rate of 20 K/min from room temperature to the set isothermal temperature in the range 873 – 1073 K (600 – 800°C).
2.3 Optical Microstructures

The partially oxidized magnetite particles were cold mounted in epoxy, vacuum impregnated and polished to a fineness of 1 μm with diamond paste to attain a flat reflecting surface for examining under the microscope. Microstructures have been captured using Light Optical Microscope (Zeiss Imager.M2m, Germany) at the magnification of 1000 X to examine the pattern of oxidation interface and growth of hematite needles.

3. Results and Discussions

3.1 Oxidation Fraction and Oxidation Rate

Oxidation of magnetite is accompanied by weight gain. For the Fe₃O₄ content of the concentrate used in this study, the theoretical or maximum weight gain percentage \(\Delta W_{\text{max}}\) magnetite particles can achieve during its oxidation to hematite is evaluated to be 3.46%. The fraction of conversion during oxidation is normalized with respect to the theoretical weight gain. Therefore, oxidation fraction \(f\) or degree of oxidation is determined as the ratio of the weight gain captured by TGA to the maximum weight gain of the magnetite particles during oxidation according to Equation 3. Thereafter, the oxidation rate corresponding to the oxidation fraction is calculated for the given thermal profile.

\[
f = \frac{(W_f - W_i) \times 100}{\Delta W_{\text{max}}} = \frac{\Delta W_{\text{TGA}}}{\Delta W_{\text{max}}}
\]  

(3)

where \(\Delta W_{\text{TGA}}\) is the percentage weight change measured during oxidation in TGA between the initial weight \(W_i\) and final weight \(W_f\) of the particles.

The profiles of oxidation fraction and oxidation rate for the magnetite particles exposed to different temperature, the partial pressure of the oxidizing gas and particle size with respect to isothermal time are shown in Figure 2. It is observed that oxidation fraction increases initially at a rapid rate to the major extent, and thereafter attains a plateau region where oxidation increases gradually at the constant oxidation rate. This infers that the oxidation of magnetite on particle scale is a two-step phenomenon, which is in line with the findings reported by several researchers (2,7,15,22,23). The degree of oxidation (fraction) is found to be increasing with isothermal temperatures (Figure 2a) from 773 to 1073 K (500°C to 800°C) as well as with the increasing \(p_{O_2}\) in the oxidizing gas from 0.05 to 0.21 (Figure 2b). On the other hand, finer particle size fractions (Figure 2c) having larger surface area attains the higher degree of oxidation as compared to the relatively coarser particle size fractions, in the order of 38 to 53 μm > 53 to 63 μm > 63 to 74 μm.
Figure 2: Oxidation Fraction and Oxidation Rate for magnetite particles with respect to (a) isothermal temperatures, (b) $p_{O_2}$ in oxidizing gas and (c) size fraction.
3.2 Kinetic Models

3.2.1 Shrinking Core Model (SCM)
The isothermal oxidation results are further analyzed with the SCM to evaluate the kinetics. According to SCM, the conversion proceeds by mass transfer of gaseous phase, chemical reaction and the solid-state diffusion kinetics, as mentioned in Equation 2. Generally, mass transfer of oxidizing gas to the particle surface is not rate limiting and that is also true when the gas flow rate is optimized with the help of starvation tests in TGA. If the chemical reaction is the dominant step, the fraction of conversion for the spherical particles with respect to time proceeds according to Equation 4, whereas, if the diffusion through the product layer is the rate controlling mechanism, the same is represented by Equation 5 \(^{(21,22)}\).

Chemical Reaction at the interface,
\[
F_R = \left[1 - (1 - f)^{\frac{2}{3}}\right] = k_R t_R
\] (4)

Diffusion through the product layer,
\[
F_S = \left[3 - 2f - 3(1 - f)^{\frac{2}{3}}\right] = k_S t_S
\] (5)

where, \(F_R\) and \(F_S\) are conversion fractions corresponding to chemical reaction and diffusion in the isothermal time \(t_R\) and \(t_S\) with the rate constants \(k_R\) and \(k_S\), respectively.

The oxidation fraction \((f)\) of magnetite particles obtained experimentally for different isothermal temperatures have been rearranged and plotted according to Equation 5 and 6 with respect to the isothermal time respectively, as shown in Figure 3. The conversion – time plots for the initial oxidation (Figure 3a) as well as the later stages (Figure 3b) fits a straight-line equation. This infers that the oxidation of magnetite particles proceeds by SCM initially dominated by chemical reaction and thereafter by diffusion through the hematite product layer. The slopes of the curve fitting Equation 4 and 5 determines the rate constant terms \((k_R\) and \(k_S)\), respectively.
Figure 3: Isothermal oxidation by Shrinking Core Model (SCM) with respect to different isothermal temperatures, $p_{O_2}$ and size fraction with (a) chemical reaction and (b) diffusion as dominant mechanisms.

Since, oxidation is a thermally activated phenomenon; the variation in the rate constant with respect to isothermal temperature is expressed by the Arrhenius equation (Equation 6) and plotted as shown in Figure 4 for each of the mechanism independently.

$$\ln(TK^{(1/\eta)}) = \ln K_0 - \frac{Q}{RT}$$  \hspace{1cm} (6)

where $Q$ is the activation energy, $K$ is the rate constant of the dominant mechanism and $K_0$ is the pre-exponential factor.

The respective slope and intercept of Equation 6 determine the activation energies for the chemical reaction and diffusion mechanism for oxidation of magnetite particles, which are found to be 31 and 76.5 kJ mol$^{-1}$, respectively.
3.2.2 Avrami Kinetic Model (AKM)

Avrami Kinetic Model (AKM) hypothesizes that the isothermal conversion or phase transformation of particles proceeds by nucleation and growth, represented by Equation 2. The results of isothermal oxidation from experiments on magnetite concentrate have also been analyzed with AKM by rearranging the Equation 2 in the form of a straight line as mentioned in Equation 7. The isothermal oxidation results plotted according to Equation 7 with respect to time for magnetite particles exposed to different temperatures, $P_{O_2}$ and size fraction are shown in Figure 5.

$$\left(\ln(-\ln(1 - f))\right) = n\ln(t) + \ln(a) \tag{7}$$
It is found that there are two straight lines with different slopes respective to initial and later stages of oxidation for experiments with all the variables. It infers that the isothermal oxidation of magnetite concentrate investigated in this study satisfies AKM. Further, Avrami rate constant \(a\) for different isothermal experiments is related to Arrhenius rate constant \(K\) according to Equation 8. Thereafter, Arrhenius equation (Equation 6) is plotted for the nucleation and growth mechanisms, as shown in Figure 6, to estimate activation energies \(Q\) and pre-exponential factors \(K_0\) by evaluating the respective slopes and intercepts.

\[
K = a^n
\]  

\(8\)

![Figure 6: Arrhenius plots for Avrami Kinetic Model (AKM) for (a) nucleation and (b) growth mechanisms during oxidation of magnetite concentrate](image)

Activation energies estimated for nucleation and growth mechanisms are 15 and 226 kJ mol\(^{-1}\), respectively. Therefore, it can be postulated that during oxidation, the hematite (Fe\(_2\)O\(_3\)) crystals grow by solid-state diffusion of oxidizing gas into the matrix of magnetite (Fe\(_3\)O\(_4\)) particles\(^{23}\). Although, there might exist some uncertainties in the initial few seconds of the initial stage because of too few data points and stabilization of experimental data or response of the weighing balance to the weight gain. Therefore, the further analysis is focused primarily on the later stage of oxidation reaction to determine the kinetics.

The pre-exponential factor \(K_0\) and Avrami time exponent \(n\) determined from the Arrhenius equation (Equation 6) and the slopes of Equation 7, respectively, are tabulated in Table II. The pre-exponential factor \(K_0\) is found to vary with \(p_{O_2}\) and \(d_p\) according to Equation 9 and 10, respectively. Whereas, the time exponent \(n\) is found to increase linearly with respect to the
temperature and decreases with $p_{O_2}$ in oxidizing gas as per the Equation 11 and 12, respectively, whereas it does not vary with the size fraction of particles.

\[
K_0 = 2.81 \times 10^9 p_{O_2} + 7.511 \times 10^8 \quad (9) \\
K_0 = -6.054 \times 10^{13} d_p + 4.024 \times 10^9 \quad (10) \\
n = 4.938 \times 10^{-4} T - 0.197 \quad (11) \\
n = -0.428 p_{O_2} + 0.3231 \quad (12)
\]

3.3 Predicting Isothermal Oxidation – comparison between SCM and AKM

The kinetic parameters derived have been used further to predict the isothermal oxidation behavior of the magnetite concentrate. The oxidation fraction of the concentrate is predicted according to both the abovementioned kinetic models by utilizing the respective governing equations, such as Equation 1 for SCM (assuming mass transfer is not rate limiting) and Equation 2 for AKM. The predicted profiles of oxidation fraction ($f$) for different isothermal temperatures with respect to time are validated with the respective experimental behavior, as shown in Figure 7.

![Figure 7: Predicted and experimental isothermal oxidation of magnetite concentrate (38 – 53 μm) according to (a) Shrinking Core Model and (b) Avrami Kinetic Model](image)
It can be seen that the oxidation profiles predicted from AKM (Figure 7 b) are significantly in better agreement with the experimental observations as compared to those predicted from SCM (Figure 7 a). Further, the optical microstructures of magnetite particles (38 – 53 μm) which are oxidized at the isothermal temperature of 873 K (600°C) and 1073 K (800°C) for 60 minutes are examined, as shown in Figure 8. It is observed that the oxidation proceeds inwards from the surface of the magnetite particle by nucleation of needle-like hematite crystals which begins to grow along the preferred planes in the magnetite at the lower temperature (873 K (600°C)). Similar findings have been observed by Monazam et. al (7,23). As the extent or fraction of oxidation increases at higher temperatures (1073 K (800°C)), it seems that there is a sharp reaction interface which progresses inwards somewhat in an anisotropic manner albeit hematite needles grow significantly ahead of reaction interface into the matrix of magnetite particle. The similar observation was reported by Monsen et. al (15). Thus, it can be substantiated that the oxidation of magnetite particles considered in this study proceeds by the nucleation and growth, where the growth of hematite needles into magnetite particles occurs via solid-state diffusion mechanism. These findings are also consistent for particles exposed to different $p_{O_2}$ and $d_p$.

Furthermore, the values of activation energy estimated by the SCM in this study for diffusion stage is 76.1 kJ mol$^{-1}$. Activation energies in the similar range have been found by Cho (22) by adopting the SCM. The cause for lower activation energies in regards to solid-state diffusion was attributed to the short circuit path or grain boundary diffusion. Whereas, significantly higher activation energy values such as 242 kJ mol$^{-1}$, 208 kJ mol$^{-1}$ and 469 kJ mol$^{-1}$ have been reported by Himmel (26), Päidassi (27) and Davies (28), respectively, for the solid-state diffusion mechanism. However, the activation energy determined by AKM for the growth stage in this study is 226 kJ mol$^{-1}$, which falls in the range of values reported in literature (26-28). Also, this is

![Figure 8: Light Optical Microstructures of magnetite particles (38 – 53 μm) at the magnification of 1000 X oxidized at an isothermal temperature of (a) 873 K (600°C) and 1073 K (800°C) showing hematite needles (H) growing into the magnetite matrix (M) ](image)
well backed up by the predicted profiles for oxidation fraction by AKM which matches fairly
good with that obtained experimentally (Figure 7) as well as by the microstructural observation
of hematite crystal growth ahead of reaction interface (Figure 8). Therefore, from the prospect
of activation energy values, predicted oxidation profiles and microstructural observations, it is
pursued that AKM suitably describes the oxidation mechanisms of magnetite concentrate.
Hence, AKM is adopted for further predicting the oxidation behavior of magnetite concentrate.

3.4 Non-Isothermal Oxidation Prediction using Kinetic Parameters

The kinetic parameters derived from the isothermal studies using AKM is extended to predict
the non-isothermal oxidation behavior of magnetite concentrate. This has been done by
discretizing the entire non-isothermal (time-temperature) plot with several small pseudo
isothermal steps. The variation in oxidation fraction \( f \) can be obtained from the temporal
variation of temperature and the corresponding Avrami coefficients \( (a, n) \), using Equation 2 by
marching in time for the sufficiently small step of \( \Delta t \).

In order to develop the oxidation model which should be capable enough to consider all three
parameters as variables, the kinetic parameters \( (n, K_0) \) have been correlated with the parameters
to have the combined effect in the range considered in this study. The Avrami time exponent
\( (n) \) is a function of \( T \) and \( p_{O_2} \), whereas, the pre-exponential factor \( (K_0) \) is dependent on \( p_{O_2} \)
and \( d_p \). These coefficients are correlated to their parameters in a bilinear way using least square
fitting method according to Equation 13 and 14, respectively.

\[
\begin{align*}
n &= 1.76 \times 10^{-4} T + 0.1255 \ln(p_{O_2}) - 2.03 \times 10^{-4} T \ln(p_{O_2}) \\
\log_{10} K_0 &= 11.46 + 0.786 p_{O_2} - 5.55 \times 10^{-4} d_p
\end{align*}
\]

Further, these predictions have been validated by the non-isothermal oxidation experiments.
The magnetite concentrate in the size fraction of 38 to 53 μm \( (d_p = 45.5 \mu m) \) have been
oxidized non-isothermally from room temperature to different isothermal temperatures (873 K
(600°C), 973 (700°C) and 1073 (800°C) at a heating rate of 20 K/min with 21% O\(_2\) in the
oxidizing gas \( (p_{O_2} = 0.21 \text{ atm}) \) at a flow rate of 200 ml/ min. The predicted non-isothermal
oxidation profiles have been plotted along with the experimental profiles for validation, and are
shown in Figure 9.
The figure shows that there is a kink at approximately $f = 0.55 – 0.65\%$ around the temperature of 723 K (450°C). Similar observations have been reported earlier (2,13,29,30), and it has been postulated that it is due to the formation of $\gamma$-Fe$_2$O$_3$ (maghemite) at lower temperatures, and further to $\alpha$-Fe$_2$O$_3$ (hematite) at relatively higher temperatures (say 873 K (600°C)). However, the metastable nature of $\gamma$-Fe$_2$O$_3$ makes it difficult to substantiate by means of characterization. It is observed that the predicted oxidation profiles satisfactorily follow the experimental oxidation profiles with respect to the pattern or progress of oxidation curves. Although, it can also be inferred that there is a slight deviation from model predictions in regards to the absolute extent of oxidation fraction. The values of $n, K'$, which significantly affects the oxidation behavior have been fine-tuned to estimate the range where predictions are statistically accepted. Optimizing these by least square fit enables to generate the non-isothermal oxidation predictions for entire thermal profiles within 90% confidence interval (CI).

The deviations from the experimental observations could be attributed to the fact that shape of particles within each narrow size fraction is not uniform and spherical. Another limitation could be because of the lack of experiments at different temperatures for the range of $pO_2$ and size fractions while determining the kinetic parameters. Although these experiments were not in this scope of study but incorporating them will increase the window of experimental observations, which could improve the model efficiency, and can be considered in future studies. In future, the particle kinetics and model developed in this study will be utilized to upscale and develop
the oxidation model for magnetite at pellet scale. This will be communicated later, which will provide the overall oxidation behavior of magnetite at pellet as well as at particle scale.

4. Conclusions

Oxidation behavior of magnetite has been successfully investigated quantitatively at particle scale using TGA. The study was focused on the narrow size fractions of magnetite. Isothermal oxidation kinetics have been determined experimentally by considering parameters – isothermal temperature, the partial pressure of oxygen in oxidizing gas and size fraction of particles, as variables. Experimental results have been analyzed by two kinetic models, namely, Shrinking Core Model (SCM) and Avrami Kinetic Model (AKM). Isothermal oxidation for magnetite concentrate was predicted and validated for both the kinetic models. It was found that oxidation of magnetite concentrate was comprehensively described by Avrami Kinetic Model. It postulates that the oxidation at particle scale proceeds by nucleation and growth at initial and later stages, respectively, where the growth is by diffusion mechanisms. A methodology has been developed to predict the oxidation behavior of magnetite concentrate under non-isothermal conditions and validated by experiments.

Acknowledgement

Authors thank the Hjalmar Lundbohm Research Centre (HLRC) for their financial support. We also thank Ola Eriksson and Daniel Marjavaara from LKAB for their technical inputs. Authors would also extend their sincere thanks to Prof. N. B. Ballal and Prof. M. P. Gururajan of Indian Institute of Technology (IIT) Bombay for valuable discussions.
### List of Symbols:

- $k_m$: Rate constant for mass transfer of gas
- $k_R$: Rate constant for chemical reaction at the interface
- $k_S$: Rate constant for diffusion
- $D_{ES}$: Diffusivity
- $r$: Average radii of the particles in the concentrate
- $d_p$: Average diameter of particle in the concentrate
- $p_{O_2}$: Partial pressure of oxygen in oxidizing gas
- $T$: Isothermal temperature
- $W_i$: Initial weight of concentrate in TGA
- $W_f$: Final weight of concentrate in TGA
- $\Delta W_{TGA}$: Weight change during oxidation in TGA
- $f$: Fraction of conversion by oxidation for the concentrate
- $C$: Concentration of oxidizing gas in the pellet
- $M$: Molar mass
- $\rho_B$: Bulk density
- $t$: Isothermal time
- $a$: Avrami rate constant
- $n$: Avrami time exponent
- $F_R$: Fraction of conversion due to chemical reaction at the interface
- $F_S$: Fraction of conversion due to diffusion
- $t_R$: Isothermal time to reach $F_R$
- $t_S$: Isothermal time to reach $F_S$
- $K$: Arrhenius reaction rate constant
- $K_0$: Pre-exponential factor
- $Q$: Activation energy
- $R$: Ideal gas constant
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Table I: Experimental design for the oxidation of magnetite particles in TGA

<table>
<thead>
<tr>
<th>Particle Experiment</th>
<th>$T$, K (°C)</th>
<th>$p_{O_2}$ (atm)</th>
<th>Size Fraction, $d_{p}$ (µm)</th>
<th>H.R., (K/min)</th>
</tr>
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<tbody>
<tr>
<td>P1</td>
<td>773 (500)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P2</td>
<td>823 (550)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P3</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P4</td>
<td>923 (650)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P5</td>
<td>973 (700)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P6</td>
<td>1023 (750)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P7</td>
<td>1073 (800)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P8</td>
<td>873 (600)</td>
<td>0.05</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P9</td>
<td>873 (600)</td>
<td>0.10</td>
<td>38 to 53</td>
<td>-</td>
</tr>
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<td>P10</td>
<td>873 (600)</td>
<td>0.15</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P11</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P12</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P3</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>-</td>
</tr>
<tr>
<td>P13</td>
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<td>0.21</td>
<td>38 to 53</td>
<td>20</td>
</tr>
<tr>
<td>P14</td>
<td>973 (700)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>20</td>
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<tr>
<td>P15</td>
<td>1073 (800)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>20</td>
</tr>
</tbody>
</table>

Table II: Pre-exponential ($K_0$) and time exponent ($n$) determined by AKM for magnetite particle oxidation experiments

<table>
<thead>
<tr>
<th>Particle Experiment</th>
<th>$T$, K (°C)</th>
<th>$p_{O_2}$ (atm)</th>
<th>Size Fraction, $d_{p}$ (µm)</th>
<th>$K_0 \times 10^4$, s$^{-1}$</th>
<th>$n$</th>
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<tbody>
<tr>
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<td>38 to 53</td>
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<tr>
<td>P2</td>
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<td>0.21</td>
<td>38 to 53</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>923 (650)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>973 (700)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>CI = (1.9, 21.3)</td>
<td></td>
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<tr>
<td>P6</td>
<td>1023 (750)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>P7</td>
<td>1073 (800)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>P8</td>
<td>873 (600)</td>
<td>0.05</td>
<td>38 to 53</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>P9</td>
<td>873 (600)</td>
<td>0.10</td>
<td>38 to 53</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>P10</td>
<td>873 (600)</td>
<td>0.15</td>
<td>38 to 53</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>P11</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.23</td>
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</tr>
<tr>
<td>P12</td>
<td>873 (600)</td>
<td>0.21</td>
<td>38 to 53</td>
<td>0.24</td>
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</tbody>
</table>
Paper V
Developing the Oxidation Kinetic Model for Magnetite Pellet

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Abstract

Oxidation is a vital phenomenon for magnetite pellets in their excursion through the furnace during induration. One of the pre-requisites for magnetite pellets to achieve homogeneously structured good quality pellets is to have complete oxidation before the sintering begins. It is essential to have the optimum thermal and gaseous profiles to attain completely oxidized pellets. Else, the partially oxidized magnetite pellets upon sintering might result in inhomogeneous structured pellets which could be detrimental to the quality. It is necessary to understand the mechanisms responsible for magnetite oxidation experimentally and intends to develop the mathematical model based on their kinetics. This will assist in predicting the optimum temperature profile and gas compositions for the particular mean particle size to produce homogeneous and good quality pellets on the consistent basis.

The oxidation of pellet is largely influenced by the oxidation kinetics of particles and hence studied at particle as well as at pellet scale. The principles of Grain Model have been adopted to develop the Oxidation Model at pellet scale whereas the particles oxidation follows the Avrami Kinetic Model. Oxidation experiments were performed isothermally at different temperatures in the Thermo Gravimetric Analyzer (TGA). It was found that the rate of oxidation of magnetite at pellet scale compromises of two peaks, and were complemented well by oxidation rates predicted from the model. Further, the pellet is investigated microstructurally at pellet and particle scale to substantiate the findings from the experiments and the model. The oxidation model developed is used to predict the progression of oxidation in the magnetite pellet with respect to the reaction time at three different temperatures (873, 973 and 1073 K (600, 700 and 800°C)) and at four levels of oxygen (0.21, 0.30, 0.60 and 1.00 atm) in the oxidizing gas.

Key Words

Oxidation Model, Magnetite Pellets, Thermo Gravimetric Analysis (TGA), Grain Model, Oxygen Enrichment, Microstructure
1. Introduction

Pelletization is one of the important processes of the iron and steelmaking operations for sustainable and effective use of raw materials. It utilizes the crushed, beneficiated and ground iron ore fines from the mines, and agglomerates them into spherical pellets. These pellets are heat hardened or indurated to impart sufficient strength. Iron ore pellets provide several benefits over other ferrous burdens in terms of strength and reducibility, whereas magnetite pellets offer advantages in terms of energy due to the exothermic nature of its oxidation to hematite during induration (1). The moist magnetite concentrate is mixed with additives such as flux and binder (bentonite) to produce green pellets. Thereafter, the magnetite green pellets undergo physicochemical changes during induration primarily by oxidation at low temperatures (573 – 1073 K (300 – 800°C)) and sintering at higher temperatures (> 1273 K (1000°C)) (1,2).

Ideally, it is desirable to have complete oxidation before the start of sintering to achieve best pellet properties (2,3). Though it is not the case often; partially oxidized pellet consisting of hematite shell and magnetite core begins to sinter hampering complete oxidation. This heterogeneity in the pellet structure might develop stresses owing to the difference in their sinter-ability and results in the inferior pellet quality (2-4). Whereas, keeping the pellet at low temperature for long residence time allowing the oxidation to complete during induration limits the production rate. This necessitates understanding the induration process in a quantitative manner and design the optimum thermal and gas composition profile which helps in achieving the desired pellet quality without compromising on the production rate. It is therefore intended to quantify both the oxidation as well as sintering phenomenon to seek the kinetics through careful experimentation and subsequently develop the model to capture the overall induration process.

In this quest, the current authors have carried out a detailed investigation of sintering kinetics and appropriate models have been developed to simulate the sintering of magnetite and oxidized magnetite (5,6). The experimental findings of sintered pellets at macroscopic level have further been substantiated by the degree of sintering evaluated microscopically (7). Subsequent to the sintering studies, the objective is now to investigate the oxidation phenomenon independently for the magnetite pellet and develop the model. Prior studies were done to understand the oxidation phenomenon of magnetite pellet, and various conceptual models were formulated (8-15). These postulated models are synonymous to the non-catalytic heterogeneous gas-solid reaction models for porous solids, namely, shrinking core model, pore diffusion, and the grain model. Researchers have adopted either of these models and investigated the reaction kinetics of porous solids experimentally, mostly limited to the pellet scale (4,13,16-21). Further, reactor scale models have been built upon considering these for reactions happening during the induration process (22-26).

Oxidation proceeds from the periphery of the pellet farther into the pellet through diffusion of oxygen. As the pellet at the scale of 10 – 12 mm consists of particles at the scale of 10 – 100 μm, locally at any location in the pellet, the oxidation occurs at the scale of a particle. Therefore, the oxidation model needs to be developed both at particle and pellet scale (10,11,15). Among the various non-catalytic gas-solid reaction models, the Particle – Pellet or Grain model is
considered to describe the oxidation phenomenon of magnetite pellets in the most appropriate manner \(^{3,9,11,12,27}\). Lately, Cho et al. \(^{28,29}\) studied the kinetics of magnetite pellet oxidation experimentally at particle scale by assuming shrinking core mechanism as well as at the pellet scale and further demonstrated the oxidation model for pellet using the grain model concept.

Earlier researchers have adopted that the reaction kinetics of individual particles proceeds topo-chemically with the formation of a sharp reaction interface \(^{2,12,13,16,28-30}\). As the reaction front proceed inwards in an individual particle the reacting gas gets consumed with the formation of the product layer within the pellet and resists further transport of the reacting gas. They opine that at the particle scale the oxidation is determined by the intrinsic reaction kinetics as well as diffusion of species through the product phase. The mechanism of this diffusion can be because of gaseous diffusion through the product layer if there are any pores in the product layer, or it can be through solid state bulk diffusion, grain boundaries diffusion or diffusion through other imperfections in the product matrix \(^{14,31-35}\). However, the activation energy obtained from the analysis using sharp interface model does not clearly point out to any of these mechanisms in isolation \(^{15,34,36}\). In a previous study, authors have also investigated the oxidation kinetics of magnetite concentrate at the particle scale experimentally and proposed a suitable model describing the phenomenon \(^{37}\). From the study, it can be inferred that the oxidation at the scale of particle or powder proceeds by nucleation and growth following Avrami mechanism, and growth of hematite into magnetite matrix is by solid-state diffusion. These findings were substantiated by the microstructural examination of partially oxidized particles. It was found that hematite crystals were growing ahead of the reaction interface further into magnetite particles from the periphery toward the center.

Therefore, in the current work, it is intended to perform the experimental investigation on the oxidation of magnetite at the pellet scale, and subsequently develop the Pellet Oxidation Model, which predicts the oxidation behavior/ progression under the given thermal and gaseous conditions. This has been carried out by adopting the principles of the grain model for gas-solid reactions at the pellet scale, integrated with the oxidation kinetics at the particle scale described by Avrami Kinetic Model (AKM). It superimposes the diffusion of oxidizing gas radially through the pores of pellet along with the local heat transfer owing to the exothermic magnetite oxidation. The oxidation experiments were performed in a Thermo Gravimetric Analyzer (TGA) for magnetite pellet exposed to three levels of constant temperatures (873 K (600°C), 973 K (700°C) and 1073 K (800°C)) and four levels of partial pressure of oxygen (0.15, 0.21, 0.30 and 1.00 atm) in the oxidizing gas. The experimental profiles for oxidation fraction and oxidation rate have been compared with those predicted by the model.
2. Methods and Materials

2.1 Raw Materials

The raw material used to prepare the pellets is a concentrate from the LKAB’s mine in Malmberget, Sweden. The concentrate contains Fe₂O₄ > 95% with Al₂O₃ and SiO₂ < 0.6%. The concentrate was mixed with 7% moisture by weight and 0.5% dosage of bentonite as a binder in a laboratory mixer (Eirich R02). The green mix was then fed to a drum pelletizer (for micro balling) of 0.8 m diameter to produce nucleation seeds of 3.55 – 5.00 mm diameter and then further balled into green pellets. The green pellets with the desired size fraction of 9 – 10 mm were collected by screening. The green pellets were dried in an oven at 423 K (150°C) overnight.

2.2 Oxidation Experiments

Oxidation of magnetite pellet is studied with the help of Thermo Gravimetric Analyzer (TGA) (Setaram 92). The TGA consists of a platinum wire basket where the magnetite green pellet is placed and suspended from the balance at the top, as shown in Figure 1.

![Figure 1: Schematic of Setaram TG92-16 Thermogravimetric Analyzer (TGA)](image-url)
The basket containing pellet is then lowered into the graphite tube furnace (inner diameter = 15 mm and height = 300 mm) with the help of an elevator. The maximum pellet size that can be used in this TGA is 10 mm in diameter, and hence the size of the pellets used in the study has been limited to 9 – 10 mm in diameter. The S-type thermocouple placed beneath the sample is used to measure the gas temperature adjacent to pellet surface. The mixture of 21 % O₂ + 79 % N₂ has been used as oxidizing gas with the help of gas mixer at a flow rate of 300 ml/min. The gas flow rate has been optimized by starvation tests for pellet oxidation. The furnace was heated up to the desired temperature at a rate of 20 K/min (20°C/min), held at that temperature for 60 minutes, and cooled at a rate of 20 K/min (20°C/min) under the oxidizing atmosphere. Oxidation experiments have been conducted at three temperature levels and partial pressure of oxygen at four levels, as mentioned in Table I. Each of the experiments have been corrected for buoyancy effect by the background test in TGA using the standard alumina ball of 10 mm in diameter exposed to the respective thermal profile. The in-situ weight gain of the pellet is continuously captured at each second by the data logger.

Table I: Experiments for the oxidation of magnetite pellets in TGA

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temp, K (°C)</th>
<th>$p_{O_2}$(atm)</th>
<th>Hold Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>873 (600)</td>
<td>0.21</td>
<td>60</td>
</tr>
<tr>
<td>P2</td>
<td>973 (700)</td>
<td>0.21</td>
<td>60</td>
</tr>
<tr>
<td>P3</td>
<td>1073 (800)</td>
<td>0.21</td>
<td>60</td>
</tr>
<tr>
<td>P4</td>
<td>873 (600)</td>
<td>0.15</td>
<td>60</td>
</tr>
<tr>
<td>P5</td>
<td>873 (600)</td>
<td>0.30</td>
<td>60</td>
</tr>
<tr>
<td>P6</td>
<td>873 (600)</td>
<td>1.00</td>
<td>60</td>
</tr>
</tbody>
</table>

Interrupted Oxidation Tests

The magnetite green pellets in the steel-wire basket were placed inside the vertical tube furnace at any oxidation temperature (say, 973 K (700°C)) and partial pressure of oxygen (say, 0.21 atm) at the flow rate of 300 ml.min⁻¹. The partially oxidized magnetite pellets were taken out from the furnace after oxidizing for 120, 240 and 480 secs. The partially oxidized magnetite pellets were quenched instantaneously by transferring into the nitrogen bath. Thereafter, the magnetite pellets oxidized have been cut in half, cold mounted in epoxy and polished to 1 μm in the diamond paste for microstructural examination.

3. Model Development

The concept of the grain model for gas-solid reaction system is utilized to develop the model for oxidation kinetics for a magnetite pellet. According to the grain model, the solid is a porous mass consisting of several particles or grains. At the pellet scale, the reacting gas diffuses through the macro-pores (between the particles or grains) from the surface toward the center.
As the reacting gas diffuses into the pellet, the particles undergo a physico-chemical reaction by consuming the reacting gas. The rate of reaction at the particle scale depends on the kinetic parameters at the particle scale as well as the local concentration of reacting gas inside the pellet \(0,15,38\).

While developing the model, it is assumed that the pellet with the average porosity of \(\epsilon\) is made up of several spherical magnetite particles with the mean particle size of \(d_p\). The magnetite pellet also contains the particles of bentonite (binder) but they are assumed to be neglected. When the pellet is exposed to the oxidation temperature, the magnetite particles oxidizes to hematite according to Equation 1 \(^1(1,2,29)\), which is exothermic in nature.

\[
\text{Fe}_3\text{O}_4 + \frac{3}{4} \text{O}_2 = \frac{3}{2} \text{Fe}_2\text{O}_3 + \Delta H; \quad \Delta H = 115 \text{ kJ mol}^{-1}
\]  

(1)

As the temperature at the pellet surface increases, the particles at the surface starts to oxidize and the diffusion of oxygen through the pores in the pellet determines the further oxidation of particles in the pellet interior. Therefore, the overall oxidation model is developed by adopting the pore diffusion kinetics of oxidizing gas, particle oxidation kinetics, and the associated heat transfer kinetics, in this sequence.

3.1. Pore Diffusion Kinetics

The oxidation of particles in the pellet is dependent on the diffusion rates of oxidizing gas through the pores in the pellet, and subsequently the mole fraction of oxygen \(X_{O_2}\) across the radial position in the pellet. As the oxygen diffuses in the pellet from the surface toward the center, it is consumed by the particles for oxidation, and hence, the mole fraction of oxygen decreases continuously. The resulting oxygen mole fraction from the magnetite particles is the input to the subsequent magnetite particles further into the pellet. The extent to which the oxygen diffuses in the pellet at the particular temperature and reaction time defines the inward progression of the oxidation front at the pellet scale.

The diffusion flux of \(O_2\) \((\dot{N}_{O_2})\) from the oxidizing gas comprising of \(O_2\) and \(N_2\) inside the pellet \(^{39}\):

\[
\dot{N}_{O_2} = -C \cdot D_{eff} \frac{d}{dr} X_{O_2} + X_{O_2}(\dot{N}_{O_2} + \dot{N}_{N_2})
\]  

(2)

where \(D_{eff}\) is effective diffusivity of oxidizing gas, \(C\) is the molar concentration of oxidizing gas, \(X_{O_2}\) is the mole fraction of \(O_2\), \(\dot{N}_{O_2}\) and \(\dot{N}_{N_2}\) are the diffusive flux of \(O_2\) and \(N_2\) in the oxidizing gas, respectively.
Since, $\dot{N}_{N_2} = 0$, therefore Equation 2 is written as in Equation 3.

$$\dot{N}_{O_2} = \frac{-D_{eff}C}{1-x_{O_2}} \frac{dx_{O_2}}{dr} \quad (3)$$

The effective diffusivity of the oxidizing gas in the pellet is a function of porosity ($\epsilon$) and tortuosity ($\tau$) of the pellet, as mentioned in Equation 4,

$$D_{eff} = D_{O_2-N_2} \left( \frac{\epsilon}{\tau} \right) \quad (4)$$

where, $D_{O_2-N_2}$ is the diffusion coefficient of the oxidizing gas.

The consumption of oxygen during its excursion through the pellet pores can be determined by the conservation of flux for the $O_2$, according to Equation 5,

$$\frac{1}{r^2} \frac{d}{dr} (r^2 \dot{N}_{O_2}) - \dot{G}(r) = 0 \quad (5)$$

The corresponding boundary conditions for $O_2$ diffusion are,

at $r = R$, $\dot{N}_{O_2} = k_{O_2} C(X_{O_2, \text{surf}} - X_{O_2, \text{atm}})$ and, at $r = 0$, $\frac{dx_{O_2}}{dr} = 0$

$$\dot{G}(r) = (\dot{N}_p) \delta_{M,Fe_3O_4} (0.25) \frac{df}{dt} \quad (6)$$

$$\dot{N}_p = \frac{(1-\epsilon)}{\frac{4}{3}(\pi d_p^3)} \quad (7)$$

where, $\dot{G}(r)$ is the number of moles of $O_2$ consumed at any radial location $r$ per unit volume of pellet per unit time and $\dot{N}_p$ is number of particles per unit volume of the pellet
3.2. Oxidation Kinetics of Particles

The oxidation kinetics of magnetite particles follows the Avrami mechanism, represented by Equation 8, as determined in the previous study has been incorporated here \(^{(37,40)}\). The rate of oxidation of particles locally at any location across the pellet depends on the mole fraction of the oxygen gas that has been diffused to the particle surface, according to Equation 9.

\[
f = (1 - e^{-\alpha t^n})
\]

\[
\frac{df}{dt} = n\alpha e^{-\alpha t^n} t^{n-1}
\]

where, \(f\) is the fraction of oxidation achieved isothermally after time \(t\), while, Avrami coefficients \(\alpha\) and \(n\) are the rate constant and the time exponent which provides an insight about the mechanism and rate of growth.

Oxidation is a thermally activated phenomenon, and hence, the degree and rate of oxidation of particles are expected to be affected by the local temperature in the pellet, according to the Arrhenius relation \(^{(36,38,39)}\). The coefficients of Avrami equation are related to Arrhenius rate constant \((K)\) according to Equation 10. Whereas, the activation energy \((Q)\) and pre-exponential factor \((K_0)\) for the range of variables studied were determined using the Arrhenius Equation as mentioned in Equation 11.

\[
K = a^n
\]

\[
\ln(TK^{(1/n)}) = \ln K_0 - \frac{Q}{RT}
\]

The activation energy was found to be 225 kJ mol\(^{-1}\) in the range of temperatures considered \(^{(37)}\). Based on experimental data an empirical relationship was obtained for the variation of \(n\) and \(K_0\) with respect to temperature, the partial pressure of oxygen and mean particle size. These equations are as follows.

\[
n = 1.76 \times 10^{-4} T + 0.1255 \ln(p_{O_2}) - 2.03 \times 10^{-4} T \ln(p_{O_2})
\]

\[
\log_{10} K_0 = 11.46 + 0.786 p_{O_2} - 5.55 \times 10^{-4} d_p
\]
The principle of superposition was used to determine the rate of oxidation under isothermal conditions as discussed in the previous study (37).

### 3.3. Heat Transfer

The heat transfer within the pellet is modelled using one dimensional conduction equation (Equation 14) given below,

\[
\frac{\rho c_p \partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 k_{\text{eff}} \frac{\partial T}{\partial r} \right) + H_{\text{gen}}
\]  

(14)

Here, \( k_{\text{eff}} \) is the effective conductivity of the pellet and \( H_{\text{gen}} \) is the exothermic heat generation due to local rate of oxidation.

Initially the whole pellet is at ambient temperature, \( t = 0, 0 < r < R, T = T_{\text{ambient}} \)

As the pellet is lowered into the furnace, the furnace temperature is assumed to be changing linearly. In the isothermal zone of the furnace, the furnace temperature is constant. The heat transfer to the pellet is primarily governed by radiative heat transfer. This is incorporated through the boundary condition, which can be written as Equation 15,

\[
-k_{\text{eff}} \frac{\partial T}{\partial r} \bigg|_{r=R} = \sigma \varepsilon \left( T_{R=R}^4 - T_{\text{furnace}}^4 \right)
\]

(15)

The effective thermal conductivity (\( k_{\text{eff}} \)) used here is determined from the experiments on thermal diffusivity (\( \alpha \)) measurements for the magnetite green pellets using Laser Flash technique (36,39,41).

### 4. Results and Discussions

#### 4.1 Input Parameters

The input parameters mentioned in Table II, the model predicts the overall oxidation fraction and rate of oxidation of the magnetite pellet. The model results also provide the distribution of temperature and mole fraction of O\(_2\) within the pellet, which helps in estimating the radial extent
of diffusion of oxidizing gas into the pellet. The model also facilitates to predict the progression of oxidation front within the magnetite pellet with respect to time for the pellets exposed to different isothermal temperatures and partial pressures of oxygen in the oxidizing gas.

Table II: Input Parameters to the Pellet Oxidation Kinetic Model

<table>
<thead>
<tr>
<th>Particle Variables</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Particle Size</td>
<td>35 X 10^-6 m</td>
</tr>
<tr>
<td>Maximum weight gain for Fe₃O₄ particles during oxidation</td>
<td>3.455 %</td>
</tr>
<tr>
<td>Magnetite Oxidation heat</td>
<td>460 kJ mol⁻¹</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>225 kJ mol⁻¹</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pellet variables</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of the pellet</td>
<td>10 X 10⁻³ m</td>
</tr>
<tr>
<td>Porosity of Pellet</td>
<td>30 %</td>
</tr>
<tr>
<td>Partial pressure of O₂ in the oxidizing gas</td>
<td>0.15 atm, 0.21 atm, 0.30 atm, 1.00 atm</td>
</tr>
<tr>
<td>Initial temperature of the pellet</td>
<td>300 K</td>
</tr>
<tr>
<td>Surrounding or Furnace temperature</td>
<td>873 K (600°C), 973 K (700°C), 1073 K (800°C)</td>
</tr>
<tr>
<td>Thermal conductivity for magnetite pellet</td>
<td>1.5 W m⁻¹K⁻¹</td>
</tr>
<tr>
<td>Emissivity of magnetite pellet (reasonable to assume near black body)</td>
<td>0.8</td>
</tr>
<tr>
<td>Mass Transfer coefficient across the pellet</td>
<td>1.02 X 10⁻²</td>
</tr>
<tr>
<td>Number of cells in the pellet</td>
<td>100</td>
</tr>
<tr>
<td>Time interval in each cell</td>
<td>0.01 sec</td>
</tr>
<tr>
<td>Holding time at isothermal temperature</td>
<td>3600 sec</td>
</tr>
</tbody>
</table>

4.2 Oxidation Fraction and Oxidation Rate for the Pellet

The overall oxidation fractions and oxidation rates for the magnetite pellets with respect to time is predicted from the pellet oxidation kinetic model, and are shown in Figure 2. The profiles have been predicted for the magnetite pellets exposed to different temperatures and partial pressures of oxygen in oxidizing gas. The predicted profiles are compared with those obtained from the oxidation experiments for pellets conducted in the TGA. The weight gain during the oxidation of magnetite pellets is converted to their corresponding fraction of oxidation ($f_{TGA}$) by equating with respect to the theoretical weight gain according to Equation 16. The theoretical
or maximum weight gain ($\Delta W_{\text{max}}$) evaluated for the pellets during oxidation of magnetite to hematite used in this study is 3.36 %.

$$f_{\text{TGA}} = \left( \frac{W_f - W_i}{W_{\text{ini}}} \right) \times 100 = \frac{\Delta W_{\text{TGA}}}{\Delta W_{\text{max}}}$$  \hspace{1cm} (16)

where $\Delta W_{\text{TGA}}$ is the percentage weight change measured during oxidation in TGA between the initial weight ($W_i$) and final weight ($W_f$) of the pellet.

The oxidation fraction of pellet increases at a rapid rate initially to the major extent, and thereafter increases gradually at a slow rate once it reaches the plateau region as shown in Figure 2 (a), this is similar to the behavior of magnetite particles as reported earlier (37). This infers that the oxidation of magnetite on pellet scale is also a two-step phenomenon, as reported previously by several researchers (2,16,28,30,42). The degree of oxidation (fraction) is found to be increasing with the temperatures from 873 to 1073 K (600°C to 800°C), whereas, the degree of oxidation tends to attain similar extent with increasing partial pressure of oxygen in the oxidizing gas at the same temperature. The predicted oxidation fraction profiles are in fair agreement at 873 K (600°C) in comparison to those determined experimentally, whereas it is over-predicting at higher temperatures at $P_{O_2}$ of 0.21 atm. However, the predicted oxidation fraction profiles for pellets exposed to different $P_{O_2}$ at 873 K (600°C) are also in fine agreement as compared to the experimental ones, but with the exception at $P_{O_2}$ of 1.00 atm, where it is being slightly over-predicted.

The rate of oxidation determined from the TGA experiments and the model, plotted as function of time at different temperatures as well as at different partial pressures of oxygen is shown in Figure 2 (b). The rate of oxidation with time obtained from the TGA experimental data shows interesting behavior; two peaks at high temperatures and at lower temperatures the second peak evolves to a plateau. This type of behavior either has not been reported or discussed for magnetite pellet oxidation in the previous studies (28,42). The model is able to capture this behavior. Though a similar behavior with oxygen partial pressures is also observed in the experimental rates of oxidation, the model has captured this behavior only to a limited extent. It should be noted that it is difficult to avoid initial transients in TGA experiments. Earlier researchers (28,42), in their TGA experiments, had allowed the magnetite pellet sample to come to uniform furnace temperature under inert atmosphere and subsequently the inert gas was switched to an oxidizing atmosphere. However, depending on the volume of the TGA reactor and flow rate of the gas, it would take some time to reach a uniform gas composition in the reactor. In the present experiments as mentioned earlier, the sample was lowered from the room temperature to the reactor zone where temperature and gas composition were already at the desired level. Here, the initial thermal transients in the pellet cannot be eliminated. Therefore, the peaks could be arising out these initial thermal transients.
Figure 2: Overall oxidation fraction and oxidation rate profiles predicted by Pellet Oxidation Kinetic Model for (a) different isothermal temperatures and (b) different partial pressure of oxygen in oxidizing gas for magnetite pellets and compared with those obtained experimentally from TGA.

In order to analyze the possible reasons for this behavior, simulation experiments were conducted. When simulations are carried out with pellet being at the furnace temperature (873 K (600°C), from the start of oxidation (please note that experimentally this was not possible, as the pellet is lowered to the high temperature zone), the rate of oxidation shows a monotonic decrease in rate of oxidation with increasing time, as depicted in Figure 3. The thermal conductivity of the pellet did not show significant variation in the rate of oxidation curves. Simulation experiments carried out without considering the heat of oxidation showed significant decrease in peaks intensity though the shapes of the curves remained similar.
However, simulation experiments with changing diffusivity of oxygen, mass transfer coefficient and pre-exponential factor for the particle kinetics changed the oxidation curves significantly. It may note that particle oxidation kinetics showed a large initial rates followed by sharp decrease in rates at higher extents of oxidation. Similarly local temperature variation due to oxidation heat can also change the rates of oxidation significantly. These effects in conjunction with diffusion of oxygen results in such non-monotonic behavior. It should be also noted that the effect of oxygen partial pressures on the particle oxidation kinetics has been experimentally obtained only for a single temperature. Possibly, more experiments on particle oxidation varying the oxygen partial pressure and temperatures can give better predictions on the pellet scale.

Figure 3: Predicted oxidation rate profiles investigating cases where (a) $T_{\text{surface}} \neq T_{\text{furnace}}$ and $\Delta H \neq 0$, (b) $T_{\text{surface}} = T_{\text{furnace}}$, (c) $\Delta H = 0$ and (d) $T_{\text{surface}} = T_{\text{furnace}}$ & $\Delta H = 0$

However, it is observed from the Figure 2 that there exists the deviation between the predicted and experimental oxidation rate curves. It is to be noted that the magnetite pellet chosen in this study for the TGA experiments consists of multi-sized particles in the desired proportion. Hence, the finer sized particles within the pellet oxidize at the rapid rate with respect to the coarser particles. It is therefore postulated that the presence of fine particles in the pellet increases the oxidation rate in the experiments as compared to that of the predicted one with mono-sized particles.

Further, in order to affirm this understanding, the microstructural investigation has been performed at both pellet scale and particle scale. For this purpose, the interrupted oxidation tests
for magnetite pellets have been designed in such a way that it can help in following the progress of oxidation front at pellet as well as particle scale.

Figure 4: Optical Microstructure of partially oxidized pellet quenched after (a) 120 sec and (b) 480 sec at 973 K (700°C) and $p_{O_2}=0.21$ atm at pellet scale and at particle scale across the radial distance at the magnification of 1000x
The optical microstructures of partially oxidized magnetite for 120 and 480 secs were captured at the pellet scale, as shown in Figure 4. The optical microstructures at particle scale across the radial distance from the surface to the oxidation front and to the center of pellet are also depicted in Figure 4. It can be seen that the pellet oxidation front observed has progressed farther into the pellet, whereas, the particle oxidation front has not yet reached to the center of the particles. This infers that the oxidation front at pellet scale and the particle scale travels at different rates. It seems that the diffusion of oxygen gas is limited beyond the pellet oxidation front, and hence, the particles did not start to oxidize. However, fine particles at the surface of the pellet are either completely oxidized or have reached to a significant extent as compared to the relatively coarser particles. This substantiates the findings postulated from the oxidation rate curves from TGA experiments as well as predicted from the pellet oxidation kinetic model.

4.3 Oxidation Front Progression within the pellets

The oxidation kinetic model developed in this study is further used to predict the progress of the oxidation of magnetite at the pellet scale across the radial distance with respect to temperature and oxygen content.

4.3.1 Elevation of Oxidation Temperature

The oxidation fraction across the radial positions in the pellet at different reaction times is predicted at the three temperatures (873, 973 and 1073 K (600, 700 and 800°C)) using the model, as shown in Figure 5. The results from the model show that the oxidation front is getting sharper with the increase in temperatures from 873 to 1073 K (600 to 800°C) after the same oxidation time for given partial pressure (0.21 atm) of oxygen in the oxidizing gas. Although, when the pellet is oxidized for a larger extent of time, the models shows that it oxidizes homogeneously across the pellet and attains higher oxidation fraction with increasing temperature.

![Figure 5: Predicted oxidation fraction across radial distance within the magnetite pellets at (a) 873 K (600°C), (b) 973 K (700°C) and (c) 1073 K (800°C) for different time intervals at \( p_{O_2} = 0.21 \) atm](image)
Figure 6: Predicted progression of oxidation front within the magnetite pellets at (a) 873 K (600°C), (b) 973 K (700°C) and (c) 1073 K (800°C) after 120, 240 and 480 seconds at $p_{O_2}$ of 0.21 atm.

The representation of the progress of magnetite oxidation on the radial plots is shown in Figure 6 for the above mentioned three temperatures after 120, 240 and 480 seconds at $p_{O_2} = 0.21$ atm. A video clip is also attached to this paper depicting the progress of oxidation for these temperatures for better realization.
4.3.2 Enrichment of Oxygen

Similarly, the oxidation fraction across the radial positions in the pellet after 120, 240 and 480 seconds is predicted by enriching the oxygen to have higher partial pressures in the oxidizing gas (0.21, 0.30, 0.60 and 1.00 atm) at 1073 K (800°C) using the model, as shown in Figure 7. The results from the model show that the oxidation proceeds rapidly to near complete oxidation in rather a homogenous manner at higher oxygen partial pressures from 0.21 to 1.00 atm in the shorter time.

![Figure 7: Predicted progression of oxidation front within the magnetite pellets at 873 K (600°C) after 120, 240 and 480 seconds of oxidation at $p_{O_2}$ of (a) 0.21 atm, (b) 0.30 atm, (c) 0.60 atm and (d) 1 atm](image)

Thus, it can be considered that the developed oxidation model for magnetite at pellet scale is successfully capturing the entire oxidation phenomenon during induration. This will further help in designing the thermal and gaseous profile necessary to achieve the homogenously oxidized magnetite pellets before the sintering starts and enable to produce good quality indurated pellets on the consistent basis. According to the model output, it is proposed that the complete and homogeneous oxidation of magnetite pellets can be obtained either by elevating
the oxidizing temperature to 973 K – 1073 K (700°C – 800°C) or by oxygen enrichment (60% or 100% O₂) or by the combination of both.

In future, it is planned to incorporate the effect of multi-sized particle distribution at each cell layer into the pellet oxidation model. This will help in refining the model and further improves its efficiency. Additionally, it is also intended to integrate the kinetic oxidation model developed in this study with the sintering models derived earlier (5,6) to develop the overall comprehensive Single Pellet Induration Model (SPIM) for magnetite pellet.

5. Conclusions

The oxidation phenomenon for magnetite at a pellet scale has been investigated experimentally and a mathematical model is developed successfully in this study. The Pellet Oxidation Kinetic Model is built on the approach outlined by the Grain Model for gas-solid reaction kinetics, by incorporating the Avrami Kinetic Model for oxidation kinetics at particle scale. The experiments have been conducted at three isothermal temperatures (873, 973 and 1073 K (600, 700 and 800°C)) and four levels of partial pressure oxygen (0.15, 0.21, 0.30 and 1.00 atm) in the oxidizing gas. The experiments showed that the oxidation rate curves possess two peaks with the peak intensity increases with temperature, whereas they marginally increase with respect to the partial pressure of oxygen. The same has been complemented well by the results predicted from the pellet oxidation kinetic model. The deviation in the predicted oxidation rate curves from the experiment could be because of the rapid oxidation of fine particles from the distribution of multi-sized particles present in pellet, instead of mono-sized particles. These findings have been substantiated by the microstructural investigation at pellet and particle scale.

The model is further used to predict the progress of oxidation front into the pellet, which is exposed to different temperature and oxygen levels in the oxidizing gas. It is found that when the magnetite pellet is being oxidized at the temperature of 973 K – 1073 K (700°C – 800°C) at 21% O₂ or by enriching the oxygen levels (60% or 100% O₂) at 1073 K (800°C) or by the combination of both can achieve complete oxidation in the minimum possible time.

Acknowledgment

Authors thank the Hjalmar Lundbohm Research Centre (HLRC) for their financial support. We also thank Ola Eriksson and Daniel Marjavaara of LKAB for their technical inputs. Thanks are due to Lars-Olof Nordin and Staffan Hedvall of LKAB Metlab, Lulea, Sweden for sample preparation for microstructural study.
References


