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INVESTIGATING THE OXIDATION PHENOMENA OF MAGNETITE PELLET

Abstract

Induration of magnetite pellet is a complex physico-chemical process involving oxidation, sintering and the heat transfer phenomena. Often, these phenomena happen simultaneously and influence each other in the induration furnace. It could be because of the highly exothermic nature of oxidation phenomena that can result in significant temperature gradients inside the pellet and sintering might begin much earlier than it is ideally supposed to. This could result in the formation of pellets with heterogeneous phases and crystallographic properties such as duplex structure, and results in the inferior quality of pellets across the bed. In order to predict the optimum thermal profile to achieve homogeneous good quality pellets on a consistent basis, it is necessary to develop a model based on the kinetics of each of these phenomena. This will help to identify and optimize the responsible process parameters during induration accordingly. Subsequent to the investigation of sintering kinetics of magnetite pellets, the current study focuses on the oxidation phenomena. The reaction mechanisms for oxidation of magnetite pellets is dependent primarily on factors such as temperature and oxygen content in the oxidizing gas, etc. Isothermal oxidation of magnetite at pellet scale has been studied experimentally using Thermogravimetric Analyzer (TGA) by inserting the single pellet directly into the isothermal zone of the furnace. It has been found that the oxidation phenomena in the magnetite pellets is a multi-stage phenomena dominated by distinct mechanisms depending on varying extent of oxidation with respect to temperature and oxygen content.

Key Words

Induration, Isothermal Oxidation, Magnetite Pellet, Oxidation Rate, Thermogravimetric Analysis

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1. Introduction

Pelletizing is the leading agglomeration technique practiced across the world, especially for magnetite ore fines. Pelletizing of magnetite ore provides an added benefit in terms of energy generated from highly exothermic nature of magnetite oxidation. Swedish steel industries have pioneered in operating the blast furnaces with cent percent pellets as ferrous burden. This makes it necessary to understand the entire process of pelletization, where green pellets are strengthened through heat hardening process for subsequent use in iron making units such as blast furnace and direct reduced iron processes. Induration is carried out either in a straight grate furnace or in straight grate furnace followed by a rotary kiln furnace. The hot gases are allowed to flow upward as well as downward through the packed bed of pellets and in counter-current direction across the furnace for efficient heat transfer. During induration, magnetite pellet undergoes drying (RT – 250°C), oxidation (300 – 750°C) and sintering (> 1000°C) [1]. As the reaction front moves inwards from the surface to the center of the pellet by the diffusion of hot gases through pores, the oxidation should preferably precede the sintering. However, often in reality, because of the exothermic nature of magnetite oxidation the temperature inside the pellet rises which might cause the sintering to begin earlier than otherwise, and may proceed simultaneously with the oxidation of pellet. Depending on the extent of each of the phenomena, this might result in the formation of heterogeneous phases in the pellet, such as duplex phase with the magnetite core and hematite shell, and thus inducing stresses due to difference in the crystallographic properties of phases [1-4]. In order to achieve homogenous good quality pellets on consistent basis, developing a model that can predict the optimum thermal profile for pellets during induration could be fruitful, especially considering the variations in raw material sources in future. Therefore, it is necessary to understand the fundamentals and kinetics of the mechanisms involved in these phenomena during induration to avoid or minimize the formation of heterogeneous phases/structure in the pellets. The methodology adapted is to study each of these phenomena in isolation in order to quantify them and estimate the kinetic parameters, which can be useful in model development. In addition, this gives an insight about the dominant mechanism in the pellet. The sintering kinetics of oxidized and non-oxidized magnetite have been estimated at pellet scale in isothermal conditions, and discussed elsewhere [5,6]. Subsequent to the studying the sintering phenomena, the oxidation of magnetite at pellet scale have been investigated and discussed in this paper. Isothermal oxidation experiments have been executed with two prime parameters as variables – temperature and O₂ content in the oxidizing gas using Thermogravimetric Analyzer (TGA). The results have been presented and discussed in this paper to have comprehensive understanding of the overall oxidation phenomena for magnetite pellets.

2. Materials and Methods

The source of magnetite chosen here is pellet concentrate from Luossavaara-Kiirunavaara AB's (LKAB) mine in northern part of Sweden. The concentrate was collected carefully by coning and quartering, and contains Fe₃O₄ > 95% with Al₂O₃ and SiO₂ < 0.6% and 7% moisture by

weight. The concentrate was mixed with 0.5 % dosage of bentonite as binder in a laboratory mixer (Eirich R02). This green mix was then fed to drum pelletizer (micro balling) of 0.8 m diameter to produce nucleation seeds of 3.5 – 5 mm diameter and subsequently balled into green pellets [1]. The green pellets of desired size fraction of 9 – 10 mm were collected by screening. The green pellets were dried in an oven at 150°C overnight.

Oxidation phenomena is captured by TGA measurements (Setaram 92), and its schematic is shown in Figure 1. The pellet sample is suspended from the balance in a platinum wire basket and lowered into the graphite tube furnace with the help of an elevator. The maximum diameter of the pellet that can be run in the instrument is 10 mm, and hence the size of the pellet used for the study has been limited to 9 – 10 mm in diameter. Argon (Ar) is used as an inert gas and different proportions of O₂ in N₂ has been used as the oxidizing gas with the help of gas mixer at the flow rate of 300 ml/min. The thermal profile designed for the each of the experiments consists of heating the furnace up to the desired isothermal temperature at the rate of 20°C/min, held for 4 hours, and cool at the rate of 20°C/min under the oxidizing atmosphere. The oxidation experiments are designed considering isothermal temperatures and O₂ content as variables over the range as mentioned in Table I, in order to simulate and understand the behavior of pellets in the induration furnace. It should be mentioned that the maximum isothermal temperature considered here is 850°C even though the effect of sintering might start to interfere in the oxidation phenomena from approximately 750°C [5]. This was done to follow the oxidation behavior of magnetite pellet at the outset on the other end of spectrum. Isothermal oxidation experiments at higher O₂ content (30 % and 100%) has been designed with similar purpose. The *in-situ* weight gain of the pellet in the isothermal segment is continuously captured at every second by the data analogger, which is used for further analysis.

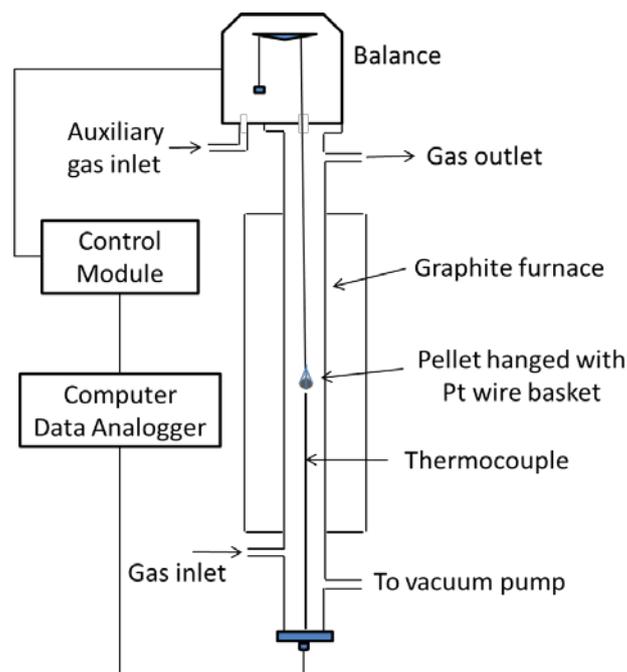


Fig. 1: Schematic of Setaram TG92-16 Thermogravimetric Analyzer (TGA)

Table I: Experimental design for the oxidation of magnetite pellets in TGA

Parameter	Temperature (°C)	O ₂ (%)
Temperature	400	21
	450	
	500	
	550	
	600	
	650	
	700	
	750	
	800	
	850	
O₂ (%)	600	5
		10
		15
		21
		30
		100

It is to be noted that unlike earlier oxidation studies, where the TGA experiments were performed by changing the carrier gas from inert to oxidizing once the furnace reaches the set isothermal temperature [3,7,8], in this study, the pellet sample have been lowered directly into the furnace already filled with the oxidizing gas at the desired O₂ content and isothermal temperature [1]. This method has been adapted to capture even the early stages of oxidation of the pellets to understand the overall oxidation phenomena, which otherwise would not have been captured. It is because when the carrier gas is changed, the oxidizing gas is diluted by the inert gas at the beginning of oxidation experiment and the initial rate of oxidation will be too low [1]. Lowering the sample elevator in the instrument takes 24 seconds, and this time is deducted from the total oxidation time. In this case, the heating might start approximately 10 seconds before the pellet reaches its final position in the hot zone, but these errors are considered marginal [1]. The TGA measurements for the pellets are corrected by their respective background corrections, which is done by running the TGA with Al₂O₃ spheres with about the same weight as the green pellet following similar thermal and gas profile.

The theoretical maximum weight gain percentage (ΔW_{max}) a magnetite pellet can achieve during its oxidation to hematite is found to be 3.35 % for the chemical composition (Fe₃O₄) and mix (bentonite and gangue) of green pellet used in this study. The oxidation fraction (f) for the pellet is determined by the ratio of the measured weight gain by TGA to the maximum weight gain of the magnetite pellet during oxidation to hematite, mentioned in Equation 1. Thereafter,

the oxidation fraction is used further analysis and estimated the rate of oxidation ($\frac{df}{dt}$) for the entire thermal profile as per Equation 2.

$$f = \frac{\left(\frac{W_f - W_i}{W_i}\right) \times 100}{\Delta W_{max}} = \frac{\Delta W_{TGA}}{\Delta W_{max}} \quad (1)$$

$$\frac{df}{dt} = \frac{(f_i - f_{i-1})}{(t_i - t_{i-1})} \quad (2)$$

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 pellet, and f_i & f_{i-1} are the oxidation fraction of pellet at time t_i & t_{i-1} , respectively.

3. Results and Discussion

3.1. Oxidation Fraction

The oxidation fraction or the degree of oxidation for the magnetite pellets exposed to different isothermal temperatures and different O₂ content in oxidizing gas with respect to time is shown in Fig. 2. The oxidation continuously increases with time under the given thermal and gaseous atmosphere. It can be observed from the oxidation fraction curves that oxidation of magnetite pellet appears to occur in two stages. In the first stage, the major extent of oxidation for each pellet in their respective conditions occurs very rapidly (< 600 seconds) as soon as the pellet reaches the hot zone in TGA furnace. Whereas, the pellet attains a plateau in the second stage of oxidation and the fraction increases by a small extent even after being kept under oxidizing atmosphere for long time.

It can also be inferred from Fig. 2 (a) that the degree of oxidation of the magnetite pellet increases with temperature from 400 – 850°C. However, increasing the isothermal temperature further will not allow the oxidation to happen independently, as sintering will come into effect at such temperatures. On the other hand, it can be depicted from Fig. 2 (b) that the pellets reached a similar degree of oxidation even with different O₂ content in oxidizing gas. Although, the decreasing time for oxidation in the first stage with increasing O₂ content suggests that the initial rapid oxidation is dependent on the amount of oxygen molecules available in bulk around magnetite pellet. Hence, the higher concentration of oxygen in the gas, the faster is the initial oxidation.

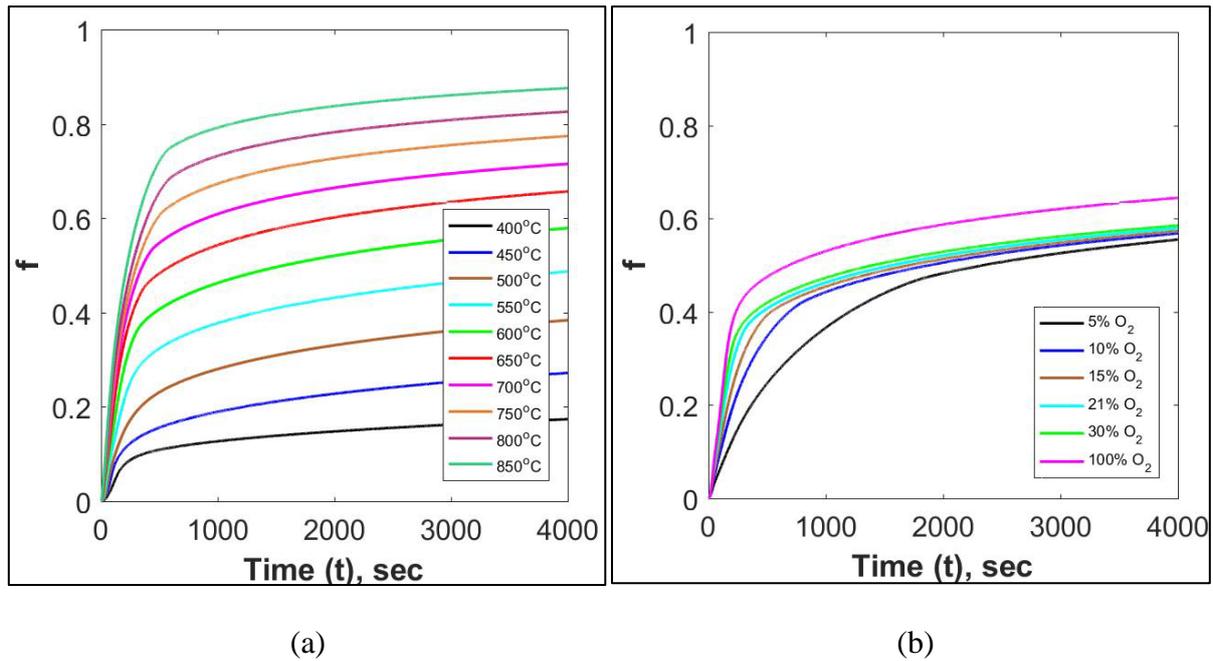


Fig. 2: Oxidation fraction profiles of magnetite pellet measured under isothermal conditions in TGA with time for (a) different isothermal temperatures and (b) different oxygen content in oxidizing gas

3.2. Oxidation Rate

The rate of oxidation profiles for magnetite pellets exposed to different isothermal temperatures and different oxygen content in oxidizing gas with respect to oxidation time are shown in Fig. 3. The oxidation rate profile for the pellet increases at the start attaining the maxima, thereafter decreases continuously as the oxidation proceeds significantly and becomes almost constant when the oxidation of pellet has reached the plateau stage. On close observation, there appears to be two peaks in Fig 3 at the early part of oxidation of magnetite pellets at higher isothermal temperatures as well as higher oxygen content. Interestingly, this type of behavior has not been observed and addressed in earlier isothermal oxidation studies on magnetite pellet [1,8]. It is quite probable that it has been surfaced because of the methodology adapted in this study to expose the pellet to isothermal atmosphere by lowering the sample in TGA. This infers that either the oxidation of magnetite pellet has an additional stage prior to regular first stage oxidation observed from the plots of oxidation fraction with time depicted in Fig. 2, or it may be due to some issues related to the instrumental set-up which authors are unable to attribute. Although, the former hypothesis seem to be more probable.

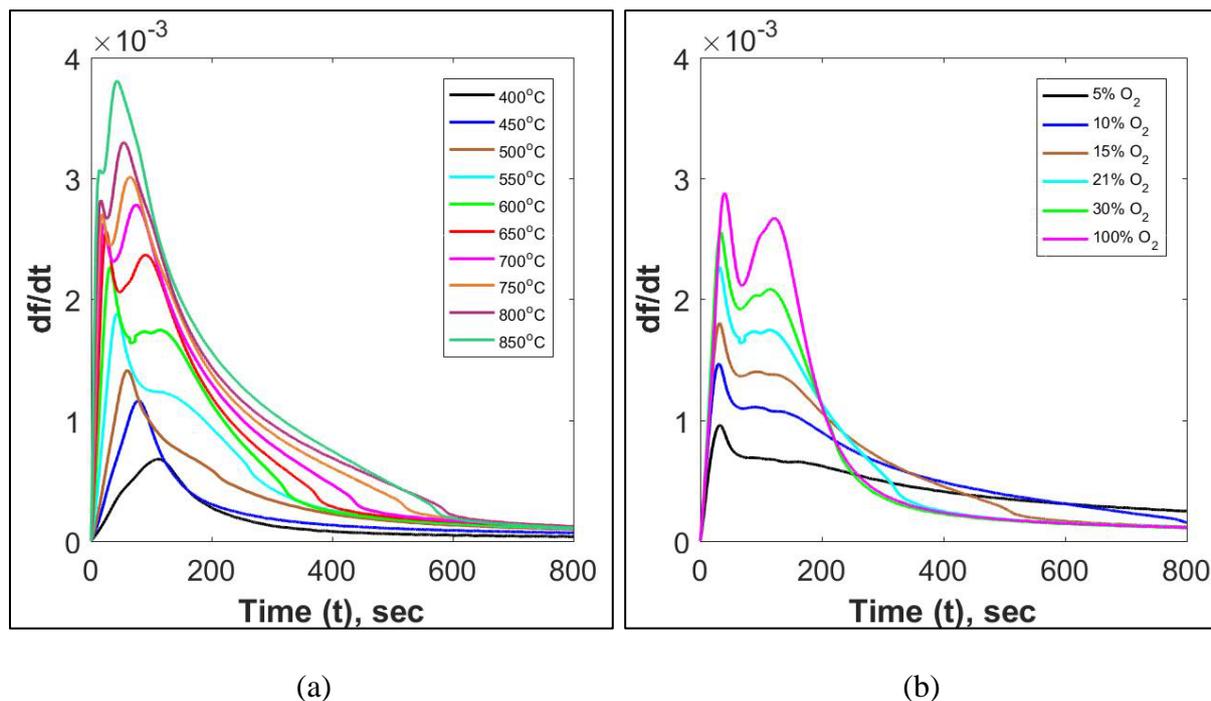


Fig. 3: Oxidation Rate profiles of magnetite pellet measured under isothermal conditions in TGA with time for (a) different isothermal temperatures and (b) different O₂ % in oxidizing gas

The oxidation rate of the magnetite pellet increases with the increase in the isothermal temperature from 400 – 850°C at 21% O₂ in oxidizing gas, as seen in Fig. 3 (a). In addition, there are few observations mentioned below that can be concluded from analyzing the appearance of two peaks in the oxidation rate curves:

- i. The two peaks appears in the magnetite pellets that are exposed to isothermal temperatures higher than 500°C. In addition, at temperatures lower than 500°C, it seem both the peaks have been suppressed together in to one major peak.
- ii. Both the peaks appears to be shifting towards lesser oxidation time with the increase in isothermal temperature, though second peak seems to be significant.
- iii. The intensity or the height of first peaks decreases with the increase in isothermal temperature, whereas that of second peak increases.

It is postulated that the appearance and intensity of the first peak could be attributed to the surface oxidation, which might have occurred due to differences in the temperature of furnace and surface of pellet for a short time as soon as it is introduced into the furnace. The higher the furnace temperature, the higher the rate at which pellet surface approaches furnace temperature and have lesser time for of instinctive surface oxidation. Thereafter, once the temperature homogenizes, the beginning of regular oxidation proceeds from the surface of the pellet inward, based on the availability of fresh reaction sites, generating the second peak. The higher the isothermal temperature the faster the oxidation of magnetite pellets.

Similarly, the oxidation rate increases with increasing O₂ content in oxidizing gas from 5 – 100% at isothermal temperature of 600°C, as shown in Fig. 3 (b). The appearance of two peaks can also be observed for the magnetite pellet exposed to oxidizing gas containing different O₂ content, except for 5% O₂. It seems that both the peaks have been suppressed in to one, as they might not be separable because of slow oxidation rate at such low O₂ content. The intensity of first peaks are more than the second peaks, and it may be because of the combined effect of high O₂ concentration and the initial temperature difference. Whereas, the intensity of second peaks increases with the increase in O₂ content whereas the peaks appear at similar isothermal time. It could be because, higher the O₂ content in the oxidizing gas, the more concentration of oxygen is available around the pellet for oxidation at rapid rate and proceed inward.

These findings infers that oxidation of magnetite pellet is a multi-stage phenomenon which could be dominated by distinct mechanisms depending on the extent of oxidation pellet has achieved. Although to substantiate the hypothesis, the investigation on the particle scale by TGA oxidation on magnetite concentrate supported by microstructures is necessary in order to get more insight about the mechanism dominating the magnetite oxidation and will be communicated in future.

4. Conclusion

The oxidation phenomena of magnetite pellets have been studied isothermal using TGA. The effect of the two prime variable parameters – isothermal temperature and O₂ content in the oxidizing gas on the oxidation is studied. The oxidation fraction is found to increase with increase in the isothermal temperature, and similar for different O₂ content. The overall oxidation rate is found to be increasing with isothermal temperature as well as O₂ content. It is also found that there appears to be two peaks in the oxidation rate profile, and suggests that the oxidation of magnetite pellet is a multi-stage phenomenon dominated by distinct mechanisms. It has been postulated that the appearance of two peaks could be attributed to the surface oxidation because of the difference in the temperatures of the furnace and the pellet initially and to the regular oxidation. Further investigation on particle scale is necessary to substantiate the hypothesis and gain more insights about the mechanisms that are dominant during the phenomena of magnetite oxidation.

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