The role of thermal improvements in indurating machines for pellet production from high-sulfur magnetite concentrate

Mehdi Alizadeh¹ · Mohsen Alizadeh² · Siavash Adhami¹

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Abstract

Mostly, magnetite iron ore mine materials contain significant amounts of sulfur base components. This can cause disturbance in production process of steel. Although high-sulfur magnetite concentrate has not been inciting enough yet to be employed by steel industry, these compounds are potential alternatives for iron ore resources. In this work, oxidation and sulfur removal of magnetite iron ore pellets were studied during the thermal treatment in the pelletizing indurating machine. The oxidation phenomenon and sulfur removal, in the magnetite iron ore pellets, were assessed by determination of appropriate thermal conditions employing thermogravimetric as well as differential scanning calorimetric tests accompanied by heat treatment procedure in a laboratory furnace. The residual sulfur-based compounds were considered as an indicator for the reaction rate; the results showed the reaction progress had a lower rate in the temperature range of 500–750 °C. Furthermore, the high-rate pre-heating and firing processes of pellets caused a higher level of residual magnetite phase within the microstructure, whereas crack initiation and growth were probable within the oxide pellets. The findings did highlight the role of thermal profiling and eventually, led to redesigning the thermal profile for pelletizing indurating machines.

Keywords FeO · Magnetite concentrate · Magnetite oxidation · Sulfur removal · Thermal analysis · Resources conservation

1 Introduction

The scarcity of iron ore concentrate resources is a real fact, and a search for alternative resources seems to be unavoidable [1, 2]. For many years, magnetite iron ore mines, containing high-sulfur content (up to 2.0%), were not very welcomed in steel industry; however, they are nowadays increasingly receiving attention as potential sources and promising alternatives for iron ore resources. On the other hand, as the open pits mining grow deeper, magnetite iron ore is gradually being replaced by sulfur containing iron ore [3]. In fact, the amount of the sulfur compounds on the top of mine is reduced as a result of the direct exposure to the air [4]. It is known that the iron recovery by

conventional method is not economically acceptable. Moreover, pretreatment of the sulfur containing iron ore will increase the processing costs. It is estimated that most of the magnetite iron ore will be consumed within a few years. Consequently, it will be crucial for the industry to adopt the offered innovative processing technologies.

As known, in order to produce green pellets, bentonite binder (< 1 wt%) and moisture (8–9 wt%) is added to the iron ore concentrates powder with particle size of less than 45 microns. Then, the mixture of raw materials is transformed into the 9–16 mm diameter green pellet by balling disk [5]. The qualified green pellets are then placed in the indurating machine which includes drying, pre-heating and firing zones [6].

✉ Siavash Adhami, adhami@gmail.com; Mehdi Alizadeh, alizadeh@cc.iut.ac.ir | ¹Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran. ²Research Institute for Steel, Isfahan University of Technology, Isfahan, Iran.

Sulfur mostly appears as “Pyrite (FeS_2)” in the magnetite iron ore concentrates [7, 8]. This mineral compound is ideally removed during the beneficiation of iron ores, since it is usually considered to be worthless (i.e., gangue type) [4].

High-sulfur magnetite concentrate can be used as a raw material for pelletizing process in iron-making industry; and sulfur removal can occur in the indurating machine via roasting phenomenon. Steel industry has shown a demand to utilize high-sulfur magnetite concentrates due to its disadvantages for the steel productions [9]. A remarkable amount of sulfur (SO_2 gas) is removed within the pre-heating and firing zones in the indurating process [2, 10–13]. Therefore, SO_2 emission, from the pellets, leads to increase in their porosities, eventually leading to the lower cold compression strength (CCS) of fired pellets [2, 9, 14]. In order to compensate the strength loss, more bentonite should be added to the mixed raw materials [15]. However, addition of bentonite, in the higher amounts, decreases the iron grade and increases the steel-making production costs [5, 16]. Furthermore, the presence of pyrite cinder in the iron ore causes an increment of the required moisture for pelletizing [6]. High water content may also cause cracks as a result of the faster drying rate [17].

The sequence of desulfurization and magnetite oxidation can affect the quality of the fired pellets, specifically in terms of CCS and residual FeO [17]. The simultaneity of magnetite oxidation and desulfurization may result in crack initiation and a dual phase pattern within the pellet structure [10, 11]. In order to improve the quality of the fired pellets, it is necessary to study sulfur elimination process from magnetite iron ore pellets from thermodynamics and kinetics point of views.

The kinetics of the sulfur removal reaction is a function of oxygen diffusion into the pellet as well as the outflow of the reaction product (SO_2). Although if the pellet soaking time at critical temperatures is not controlled, oxidation process of magnetite in the pellet core is delayed during the sintering process. In this case, surface shell of pellet is completely oxidized to hematite while the pellet core is magnetite. Therefore, stressful two-phase structures with micro-cracks are created in the pellet during the heat treatment process [3, 11]. In this regard, the furnace conditions should be controlled somehow; in which, all considerations related to the complete oxidation of magnetite and facilitation of sulfur removal are in most favorable conditions.

Assessment of sulfur contents of concentrate, which can disturb the pellet properties, were studied by Chun et al. [9], where it was shown that sulfur mainly exists in the

form of elementary sulfur in pyrite cinder, and more than 95% sulfur in raw materials is removed under the optimum firing conditions at 1230 °C for 15 min. Moreover, Zhu et al. [14] studied the effect of utilization of pyrite cinder in iron ore pellets. They suggested that the appropriate green pellets were obtained when 50% pyrite cinder and 50% magnetite concentrate were mixed together. Furthermore, they declared that 62.53% of total Fe and 0.009% sulfur content were achievable when dried pellets were preheated at 900 °C for 9 min and roasted at 1200 °C for 15 min. Forsmo et al. [10] investigated the oxidation mechanisms of the magnetite iron ore green pellets concluding the rate of oxidation fallen at 1200 °C as the magnetite core seems to be heavily sintered at this temperature.

In the previous researches, mostly the effects of varying temperatures and times on the desulfurization and oxidation of magnetite iron ore pellets were investigated individually during the indurating process [9, 18, 19], while the effect of simultaneous sulfur elimination and magnetite oxidation reactions on the microstructure and the pellet quality is somehow neglected.

As mentioned above, the simultaneous sulfur elimination and magnetite oxidation in the preheating zone of the indurating machine will have a deteriorating effect on the pellet quality. This can be avoided by identifying the kinetics of both of the mentioned reactions and offering an appropriate thermal profile of the furnace. In the present work, the magnetite oxidation reaction as well as sulfur removal in the magnetite iron ore pellets were studied from thermodynamics and kinetics point of views, by using thermal analysis and simulation of pre-heating zone of pellet indurating machine, leading to an innovative design in thermal profile for this purpose.

2 Experimental

The examined iron ore pellets were provided by Gol Gohar Mining and Industrial Co, Sirjan, Iran. The utilized green pellets consisted of approximately 85 wt% magnetite, 8.8 wt% moisture and 0.9 wt% bentonite with a plate water absorbance (PWA) of 809 and particle size of less than 45 μm . The chemical composition of magnetite iron ore concentrates is given in Table 1. The green pellets were produced in a 7.5 m diameter balling disks with rotational speed of 10 rpm inclined at 45°. The green pellet drop number was studied and recorded. The average drop number of the pellets was examined to be 6. The produced

Table 1 Chemical compositions of magnetite iron ore concentrate (wt%)

Fe_{total}	FeO	SiO_2	MgO	CaO	Al_2O_3	S	C
66.2	26.5	2.3	1.9	0.5	0.3	1.7	0.12

fired pellets were screened so that specific grades [within 10–12.5 mm in diameter (Fig. 1)] were separated. Then, cold compression strength (CCS) of the pellets was measured at the room temperature (according to ASTM E 382-07).

The differential scanning calorimetry technique, METTLER-TOLEDO, was employed to investigate the extent of temperature required for different reactions occurring in the iron ore concentrate (25–600 °C). The DSC analyses, under two atmospheres (air and high purity argon flow), were carried out at the heating rate of 10 °C/min. The mentioned set up was employed to identify the temperature restrictions of the oxidation reactions specifically for the sulfur elimination reaction. The DSC analysis showed the temperature difference between the sample and an inert reference (here alumina). Thermal characterization of the powder was performed by using the Setaram differential thermal analyzer (TG/DTA) model 92 with the heating rate of 5 °C/min in the temperature range 25–600 °C in an ambient atmosphere.

The green pellets were subjected to heat treatment procedure at different temperatures for 12 min in a laboratory furnace. A K type thermocouple was employed to record the temperature of the pellets surface. An air blower (4.5 l/min) was utilized to supply the required oxygen to the furnace.

After the heat treatment process, residual sulfur was measured by CS-2000 ELTRA elemental analyzer both in core and the whole average of the pellets.

Furthermore, microstructure of the oxidized pellets was studied by the optical microscopy. The required samples for the metallography were prepared by cold mounting followed by conventional grinding and polishing

techniques. Microstructural examination of the specimens was carried out by employing the metallurgical optical microscope (PMEB-Olympus).

3 Results and discussion

Figure 2 illustrates the DSC thermal analysis diagram of magnetite iron ore concentrate samples carried out under argon and ambient atmospheres. It can be noticed that the main difference between these two diagrams are due to the involvement of oxidation reactions (sulfides roasting and magnetite oxidation). The DSC thermal analysis diagram in argon atmosphere shows the removal of free and structural moisture, as well as decomposition of carbonate components [20]. Presumably, as there was no oxygen present in this condition, oxidation reactions were hardly occurred.

However, the thermal analysis diagram, carried out under ambient atmosphere, confirms that the roasting reactions of the iron sulfides started at the temperature range of 210–330 °C. Moreover, as it can be seen, the increase in the slope happens even at the lower temperatures. This indicates the starting of the sulfur removal reactions. The reaction rate reached the maximum level at around 300–320 °C. Furthermore, it is also clear that the magnetite oxidation reactions began and continued at temperatures greater than 400 °C.

Considering the DSC plot (Fig. 2), two regions can be distinguished: the first one which can be attributed to the preliminary elimination of sulfur and structural moisture (220–320 °C). The second region can be assigned to the

Fig. 1 Oxide iron ore pellets

Fig. 2 DSC plot of the iron ore concentrate at different atmospheres

oxidation of magnetite (more than 420 °C) in the iron ore concentrate.

The TG curve, shown in Fig. 3, is in agreement with the DSC data for the intended reactions at the certain temperature ranges. As it can be seen, the first weight loss was occurred over the temperatures 220–320 °C. This can be associated to the beginning of sulfur removal process at the temperature of 220 °C; the final temperature of degradation is around 320 °C. At the higher temperature (320–420 °C), there is no significant weight change. This indicates that, at this temperature range, the only

remaining compound is Fe_3O_4 . Then, the TGA curve for the pellet showed a rise at 420 °C. According to the magnetite oxidation reaction ($2\text{Fe}_3\text{O}_4 + 0.5\text{O}_2 = 3\text{Fe}_2\text{O}_3$), magnetite is changed to hematite in presence of oxygen; which causes an increase in the weight of materials (equal to 0.5 mol oxygen gas).

The amount of the residual sulfur in both core and whole of the heat-treated pellets are shown in Fig. 4. As it can be seen, sulfur removal reaction occurred in two regions. The first region is in the temperature range of 350 to 500 °C, and the second region is in the greater range of

Fig. 3 TG curve of the iron ore concentrate under air atmosphere

800 °C. The reason for pausing or diminishing the sulfur removal reactions at temperature range of 500–750 °C can be attributed to two parameters: the occurrence of sulfur removal equilibrium reactions and the possibility of iron sulfates formation.

From thermodynamics point of view, the following reactions are in equilibrium state where FeS_2 is decomposed and simultaneously formed at the temperature range of 500–750 °C [reactions (1) and (2)] [21].

Since the equilibrium constant of the second reaction is very low ($k_{\text{eq}} = 10^{-27}$ – 10^{-28}), a slight decrease in the oxygen content can shift the reaction to the right. This is while the sulfur roasting can be conducted according to the following reaction [21]:

There is also another possible reaction [reaction (4)] at the temperatures above 500 °C, due to its exothermic nature [22]. Therefore, the removal of the sulfur partially stops at the temperature range between 500 and 750 °C.

However, because of the existence of hematite in the preheating step (magnetite will be oxidized and converted to hematite at temperatures higher than 420 °C), and due to the availability of SO_2 gas, some iron sulfates compounds can be formed, according to reactions (5) and

(6) [22]. Therefore, the presence of sulfur in the pellets is very probable which consequently leads to the formation FeO phase according to reaction (7).

Furthermore, Fig. 5 shows much wider stability range of iron sulfate samples at 500 and 600 °C compared to those at 1000 °C [23]. Therefore, the possibility of iron sulfates formation at a lower temperatures is very high which retards the sulfur elimination process at 500–700 °C. Also, it is worth mentioning that, the iron sulfate converts to hematite when temperature increases; where the SO_2 partial pressure is decreased.

The optical micrographs of both core and close to surface shell regions of the fired pellets (as-received) are shown in Fig. 6a, b, respectively. The elimination of volatile materials as well as sulfur removal from the pellets during the drying and preheating process could increase its porosity. The crack initiation, in pore wall during compression test, reduced the compression strength of the oxide pellet [24].

As Fig. 6a illustrates, the crack growth is seen at the center of the pellets. Since, from the kinetics point of view, the sulfur removal progress is a function of diffused oxygen into the pellets, and by considering the ventilation of the reaction products (SO_2), it can be concluded

Fig. 4 Effective heat treatment temperature as a function of residual sulfur

Fig. 5 The Kellogg diagram for Fe–S–O system at the temperatures typical for oxidation roasting process 500, 600 and 1000 °C [23]

Fig. 6 Microstructures of center (a) and near the surface (b) of the fired pellet (as-received); hematite phase can be seen in the bright colors; the area with gray colors represents the magnetite phase

that the comprehensive oxidation of the magnetite seems to be very unlikely. Therefore, by recrystallizing the grains and sintering the iron ore particles, the magnetite oxidation process is almost stopped in the firing zone of the furnace. In the microstructure of the pellets near the surface (Fig. 6b), the bright colored hematite phase can be observed along with the gray area representing the magnetite phases [25, 26]. Comparing these two phases, it is seen that the non-oxidized magnetite is the dominant phase in the core region of the pellets,

whereas hematite as the superiority in the regions close to the surface.

Consequently, the two-phase structure of the pellets and the differences in metallurgical behavior between these two phases, in terms of crystal lattice type and recrystallization temperature of the particles, seem to be the causes of the developing structural stresses and the non-uniform structure which occurred at the interface between the core region and the surface shell layer of the pellets [27]. These microstructural stresses can be due to

the incomplete oxidation of the pellets in the preheat zone of the furnace.

In order to have a better understanding of the effective parameters for the observed cracks in the pellets, a detailed microscopy of the microstructure was carried out (Fig. 7). The results revealed that the cracks are distributed and extended with the aid of relatively large voids.

In order to avoid the occurrence of non-uniformity, in the pellet microstructure, as well as the simultaneous

sulfur removal and magnetite oxidation, a new thermal profile for the indurating machine was introduced and applied (Fig. 8). The main advantage of this new thermal profile was to promote the magnetite oxidation at the temperature range of 500–800 °C by giving more time, and consequently providing more chance of oxygen diffusion for magnetite oxidation. It should be noted that, according to the DSC results, there is a possibility of sulfur removal in the pellet at the selected temperature range; therefore,

Fig. 7 Optical microstructure of the fired pellet (as-received)

Fig. 8 Previous induration and new schedules of iron pellet

Fig. 9 Optical microstructures of center (**a**) and near surface (**b**) of fired pellet with the new thermal profile

introducing the designed thermal profile prohibits the simultaneous occurrence of those two reactions.

The optical micrographs of both core and close to surface regions of the fired pellet with the new thermal profile (final set points) are shown in Fig. 9a, b, respectively. As can be seen, the observed cracks on the previous samples disappeared and the dual phase microstructure did not exist anymore (Fig. 9b). Moreover, the obtained chemical composition of the new-fired pellets (Table 2) clearly showed that the sulfur content and FeO phase decreased dramatically. Consequently, the average of CCS of the fired pellets increased up to 300 (kg/pellet).

4 Conclusions

The magnetite oxidation reaction as well as sulfur removal in the magnetite iron ore pellets were studied from thermodynamics and kinetics point of views in order to offer an innovative design of thermal profile in the pelletizing indurating machine.

The role of thermal improvements in indurating machines was investigated for producing pellet from high-sulfur magnetite concentrate. It was confirmed

that the roasting reactions of iron sulfides started at the temperature range of 220–320 °C, and the magnetite oxidation reactions began and continued at the higher temperatures, i.e., more than 420 °C. Considering the kinetics aspects of the mentioned phenomena, the high tendency for the sulfur removal above 800 °C resulted in a lower oxidation rate of magnetite to hematite in the iron ore pellet, which consequently led to increase in the residual FeO phase in the pellet microstructure. The sulfur removal of high-sulfur magnetite iron ore concentrates, during the pellet induration process with high heating rate in the pre-heating zone, led to crack initiation in the pellet microstructure.

The findings highlight the role of thermal improvements where the pellet properties were improved when the new thermal profile program was innovatively designed and applied. Eventually, considering the ore resources, which inevitably become unavailable in a near future, the outcome of this work suggests a reasonable approach in pretreatment process for sulfur removal and oxidizing magnetite and therefore opens up a new horizon for employing the sulfur containing iron ore by steel industry.

Table 2 Chemical compositions of fired pellet (wt%)

Fe _{total}	FeO	SiO ₂	CaO	MgO	Al ₂ O ₃	S	P
66.40	1.10	2.18	0.51	2.05	0.35	0.005	0.005

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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