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Comprehensive Utilization of Iron-Bearing Converter Wastes

Hu Long, Dong Liu, Lie-Jun Li, Ming-Hua Bai, Yanzhong Jia and Wensheng Qiu

Abstract

Basic oxygen furnace (BOF) sludge is composed of not only valuable iron but also impurities like Zn, Pb, and some alkaline oxides. It is collected from wet cleaning system in steelmaking plants. How to deal with these double identity wastes? Will the traditional landfill treatments result in environmental pollution? What technologies have been developed recently, and is it actually useful? In this chapter, physical-chemical properties and mineralogical phases of converter sludge were characterized, and different recycling technologies were introduced. The proven metalized pellet-producing process would be highlighted that green pellets made from iron-bearing sludge are dried and preheated in a traveling grate firstly, and then reduced at high temperature in a rotary kiln or a rotary hearth furnace (RHF) to get direct reduced iron (DRI), served as a good iron source for blast furnace.

Keywords: BOF sludge, iron bearing, metalized pellet, direct reduced iron, environment friendly

1. Introduction

BOF sludge is collected from wet cleaning system in steelmaking plants. It is composed of not only valuable iron but also impurities like Zn, Pb, and some alkaline oxides [1–3]. Traditional landfill treatments inevitably result in environmental pollution because of the contained heavy metal and the high pH values of water-absorbed soil [4, 5]. Sintering is another recycling way to treat the sludge as raw material for sintering ore and fed to the blast furnace (BF). However, it leads to the circulation and accumulation of zinc in BF [6, 7]. To decrease the negative effects on BF production and surrounding environment, new recycling technologies have been developed, one proven of which is the metalized pellet-producing process, that green pellets made from iron-bearing sludge are dried and preheated in a traveling grate firstly, and then reduced at high temperature in a rotary kiln or a rotary hearth furnace (RHF) to get direct reduced iron (DRI), served as a good iron source for electric arc furnace (EAF) or BF [8–10]. It is an appropriate method to recycle the valuable iron and remove the harmful elements, simultaneously improve the burden structure of BF, which attracts more and more attention of metallurgical researchers.

Green pellets should be dried before charged into the consequent preheating and reduction process, or else they are easily to be cracked or pulverized owing to drastic volatilization of moisture at a high temperature, and results in the significant drop of the permeability, which will eventually lower the metallization rate of the

products in the reduction furnace, or even make the production abnormal [11, 12]. Additionally, it has been reported that about 25% of energy for pellet induration is consumed for drying [12]. Thus, the improvement of the drying performance will be energy efficient, and also the drying mechanism of iron ore pellets made from BOF sludge is extremely important.

After dried and preheated, the mainstream approach dealing with pellets is baked first and then reduced by coal or reduction gas; another way is directly reduced so-called one-step method, one proven of which is the grate-rotary kiln process with high heat transfer efficiency, where the preheated iron-bearing material instead of fired oxide pellets directly reacts with the reductant of coal at high temperature to get direct reduced iron (DRI) [13, 14]. Compared with the traditional two-step rotary kiln, the new process is simplified and the risk of kiln accretion is reduced, because of the decreasing degradation without phase transferring from hematite to magnetite, which has been developed rapidly in China [15–17]. Metallized pellets could be used as burden for electric arc furnace (EAF) or BF, and the reduction degree, compressive strength and dezincification rate are considered as three important indicators [18–21]. They were energetically investigated by metallurgical researchers recently [9, 22, 23]. Many significant researches have been carried out to understand the reduction behavior of iron-bearing materials.

In this chapter, performances of pellets prepared from the BOF sludge are briefly presented at first and then studies on drying characteristics and reduction behavior under different conditions are introduced and compared to provide scientific guidance for recycling of secondary iron-bearing resource from BOF wastes [24–26].

2. Brief process of metallized pellet production

2.1 Two-step method

For traditional two-step method, oxidized pellets are prepared initially as raw materials for metallizing process, and then metallized pellets are produced through the direct reduction process, during which the temperature is below the melting point of the iron and the products referred to as direct reduced iron (DRI).

2.1.1 Preparation of oxidized pellets

The grate-rotary kiln producing line is considered and adopted as one of the most mature technologies, which has a strong adaptability to raw material and fuel, good quality, and low cost of production. The process consists of proportioning system, mixing, pelletizing system, green ball roller screen, and distribution, as well as grate-rotary kiln system for pellet indurations, finished product stock piling, and delivery system. The grate-kiln process flow is shown in **Figure 1**.

Concentrate fines are discharged to storage bins through the belt in the stockyard. Each concentrate store is equipped with disc feeder with frequency control and electric belt scale. Limestone and bentonite are delivered by tanker and then in a pneumatic transmission. Dust from multicyclone and electrostatic precipitators (ESP) for the main induced system is delivered by pneumatic transmission to dust bin. All the storage bins adopt weighing level gage to check material level in storage bin. The set value of charge ratio is automatically controlled and regulated by programmable logic controller (PLC) microprocessor. After all kinds of materials are compounded at a certain proportion, they are delivered directly to mixing room by the belt conveyor. Mixing room is usually equipped with a vertical mixer, which can mix materials both in micro- and macroway with high effectiveness, reliable operation, and simple maintenance. Materials mixed are

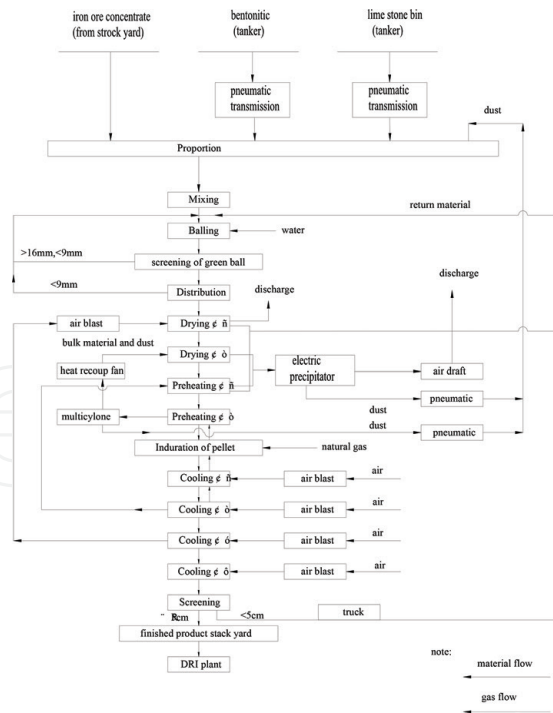


Figure 1.
 Process flow chart of grate-kiln pelletizing plant.

delivered to pelletizing room by the belt conveyor. The belt conveyor is equipped with moisture detector for check and control of water addition for palletizing.

Disk pelletizers are often adopted for preparing green pellets. Revolving speed and inclination of disk are adjustable to guarantee the quality. Roller screener is equipped for screening, and pellets with suitable size are delivered to the distributor system in chain grate room, while others that unqualified are returned by the return conveyor system.

Chain grate area is mainly consisted of shuttle-type distributor, wide belt conveyor, roller distributor, chain grate, combustion burner fan for chain grate, electric double-dumping ash valve, bucket elevator and belt conveyor, etc. Shuttle distributor discharges green pellet to wide belt conveyor under motion back and forth, and the wide belt conveyor with speed in frequency control delivers green pellets to roller distributing device. Qualified green pellets are dried and preheated in the chain grate, and delivered to rotary kiln for roasting. Chain grate is divided into four zones, which are up-draft drying zone, down-draft drying zone, preheat I zone, and preheat II zone, respectively. The thickness of material bed in chain grate is about 180–200 mm, with the normal motion speed of 3.1 m/min. Pellets are first dried in the up-draft drying section by the recycle hot air in the temperature range of 160–250°C from the third cooling zone of annular cooler, which remove attached water in green pellets and to avoid pellets in the bottom of the grate bed from wetting. Temperature of hot returning gas from the annular cooler is in the range of 180–320°C, which can be mixed with cold air if necessary. In down-draft drying zone, 320–400°C recycle hot gas from the preheating II zone is pumped by hot-resistance draught fan across material layer from upper smoke shield, which makes green pellets dehydrate and dry, and can bear high-temperature stress and strain in 550–700°C in preheating I zone. The main induced draught fan is set to pump exhausted gas from air bellow, and eliminate it into atmosphere from electric precipitator. In preheating I zone, hot gas flow continues to dry green pellets through the material layer, and dried pellets begin to be oxidized, and the heat is derived from the hot exhausted gas of annular cooler II cooling zone. In preheating II zone, pellets are heated and oxidized further, and completely indurated, which makes pellets have a certain intensity, and can bear

impact without breakage when falling to rotary kiln from chain grate in the motion of rotary kiln. Heat source comes from 900 to 1180°C hot air flow in rotary tail. A hole is left and sealed by fireclay brick in the partition wall between the first and second preheating zones. The hole can be opened in the case of thermal compensation. Hot exhausted gas in preheating I zone through collection header pipe of air bellow two sides and hot exhausted gas in down-draft drying zone are together discharged by electrostatic precipitator, main induced draught fan, and chimney. Chimney and valve are set at the top of the shield in preheating II zone, which is used for waste gas blowing off during furnace baking and emergency failure operation. Burners are installed in the cover of chain grate for thermal compensation. Preheated pellets get enough compressive, and then enter rotary kiln through kiln tail chute.

The rotary head is equipped with natural combustion apparatus with adjustable frame shape and length. Pellets are roasted while rotating in the kiln, so that the uniformity is assured. Baking temperature in rotary kiln is 1250–1320°C, revolving speed of rotary kiln is adjusted according to raw material differences to obtain enough retention time, and pellet quality. Liner made from precast brick and refractory castables makes kiln service with better thermal shock resistance and wear resistance and heat-shielding performance. An infrared simplified scanning temperature measurement system is adopted to detect and control the temperature inside. Roasted pellets are screened and discharged to receiving hopper of annular cooler.

Annular cooler consists of rotating part, air bellow, transmission device, rack, upper shield, and the system of variable-frequency adjustable-speed. It is mainly divided into four areas: I cooling zone, 900–1100°C of hot air is directly led to rotary kiln and used to raise temperature in kiln atmosphere; II cooling zone, 500–700°C of hot air returns to upper shield in preheating I zone of chain grate; III cooling zone, 180–320°C of hot air is led to up-draft drying section in grate; IV cooling section, 85–105°C of hot air is dedusted and exhausted through the chimney, with emission dust concentration below 50 mg/Nm³. Fans are adopted to cool down pellets step by step and control the temperature of hot wind, and the majority of the heat generated during this cooling process is effectively reutilized. Pellets below 120°C are discharged through the hopper to belt conveyor, and then delivered out.

2.1.2 Preparation of metallized pellets

The attempts to develop large-scale direct processes have embraced practically every known type of apparatus suitable for the purpose including pot furnaces, reverberatory furnaces, shaft furnaces, rotary and stationary kilns, rotary hearth furnaces, electric furnaces, various combination furnaces, fluidized bed reactors, and plasma reactors. Many reducing agents including coal, coke, graphite, char, distillation residues, fuel oil, tar, producer gas, coal gas, water gas, and hydrogen have also been tried. For handling the BOF wastes, coal-based direct reduction technologies including the rotary kiln or the rotary hearth furnace (RHF) are often adopted in consideration of better material adaptability as well as for steady and reliable operation.

The representative two-step coal-based rotary kiln reduction process to produce sponge iron is given below including major technical parameters, types of equipment used, and the flow of materials through the plant. It is mainly composed of coal shed, iron raw material shed, coal screening building, proportioning building, rotary kiln-cooling building, etc. Schematic flowsheet of this rotary-kiln sponge iron plant is shown in **Figure 2** [27].

The lump ore or pellet is transported into DRI plant by dump trucks. The iron raw material feeds the belt conveyor by wheel loader then delivered to the proportioning building. The reductant (coal) is transported into DRI plant by dump trucks. The

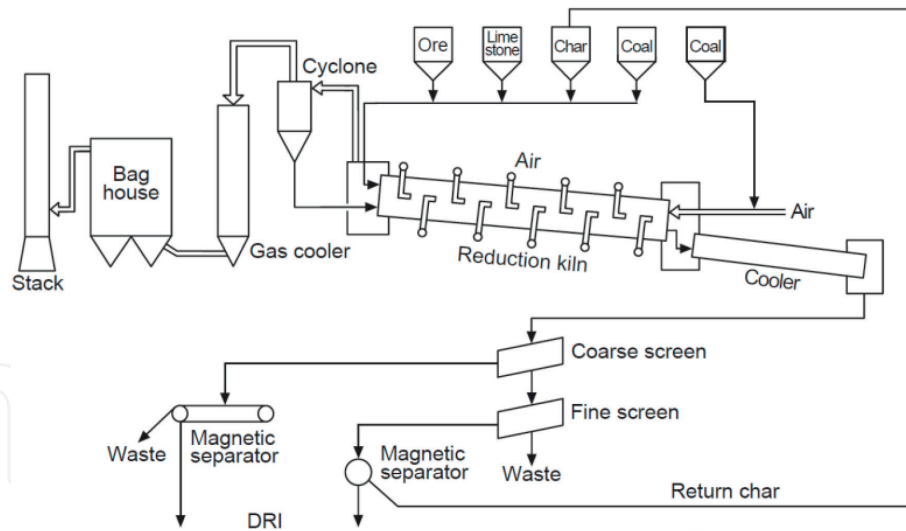


Figure 2.
Schematic flowsheet of rotary-kiln sponge iron process.

capacity of the reductant (coal) storing yard is for about 16 days. Coal is fed into the belt conveyor by wheel loader and then delivered to the coal screening building for classification. The grain size of reductant is 0–50 mm. According to the process requirement, the grain size of the coal fed at the head of rotary kiln is 3–25 mm and at the tail is 25–35 mm. The coal is separated into four granularities: 0–3, 3–25, 25–35, and 35–50 mm by linear screen. The coal with grain size 3–25 mm will be delivered to the coal hopper at the head of the rotary kiln, coal with grain size 25–35 mm is delivered to the coal bin in the proportioning building by belt conveyor, and coals with grain sizes 0–3 and 35–50 mm are delivered to power plant by truck. The desulfurizer (limestone) is transported into DRI plant by dump trucks and discharged into the receiving hopper in the proportioning building, and then delivered to the limestone bins in the proportioning building by steeply belt conveyor. The proportioning of iron raw material, limestone, and coal is completed in the proportioning building. The belt scale is adopted to make proportioning accurate.

The rotary kiln is one of the main equipments used to produce directly reduced iron products. The mixed material fed into the rotary kiln is heated up to a certain temperature in the kiln, and then the reduction reaction will take place. Detailed process is as follows. The iron raw materials, coal, and limestone used for reduction are fed at the head and tail of the rotary kiln separately. The granular coal injection gunner and the ignitor based on diesel oil will be settled in the head of rotary kiln. The diesel oil ignitor is set to increase temperature up to the range of 600–800°C. The grain size of coal fed at the head is 3–25 mm, which is injected to the rotary kiln by granular coal injection gunner. The grain size of coal fed into the rotary kiln at the tail is 25–35 mm, together with limestone and iron raw material by belt scale. According to the chemical equation $C + CO_2 = 2CO$, the CO will react with the oxygen contained in the pellet. The rest of the CO is burnt with the secondary injecting hot air to heat up the rotary kiln and the pellets. A series of chemical reactions take place with the iron raw materials, reductant, and desulfurizer, and then the oxidized pellets are reduced to metallized pellets, so-called sponge iron. The sponge iron is discharged to the cooler drum from the end of the rotary kiln. The temperature inside the rotary kiln is in the range of 1000–1100°C, and the retention time inside is about 5–9 h. After that, the sponge iron at high temperature is discharged to the fixed screen and sent to the cooler drum to be cooled.

The cooler drum is self-sealed with credible sealing device at the feed end and discharge end, and operated with micropositive pressure with the inner part isolated from the outside environment (air). To avoid oxidation, the product is cooled

down below 120°C indirectly by spraying water to the outside surface of the cooler drum. The material will stay inside for about 25–40 min.

The cooled product is delivered to the product sorting room to screening and classification in order to separate the DRI, magnetic powder, nonmagnetic powder, and return coal fines. The product discharged from the cooler drum is delivered to the screen equipment and separated into two granularities: >4 and <4 mm. To minimize the iron content in nonmagnetic powder, the product of >4 mm will be proceed in three steps in magnetic separator. The magnetic material discharged from the magnetic separator is fed to the steel melt shop. The nonmagnetic material is discharged from the bottom of magnetic separator, regarded as return coal, and delivered to proportioning building. The product of <4 mm is separated in two serial elutriator for pneumatic classification: the light one such as ash is dedusted, and the heavier one is pneumatic delivered to the single magnetic separator. After magnetic classification, the nonmagnetic powder is delivered to nonmagnetic bin by belt conveyor and bucket elevator and then transferred by trucks; the magnetic material will be separated in elutriator, delivered to magnetic bin by belt conveyor and then pressed into block, and finally delivered to the steel melt shop too.

2.2 One-step method

The “one-step” method is mainly composed of concentrate pelletizing—preheating—direct reduction (coal-based kiln reduction/rotary hearth furnace)—cooling. Compared with the traditional two-step method, the preheated pellets with certain intensity are directly delivered to the direct reduction furnace, which not only shortens the process line with satisfactory product quality, but also saves the energy.

The key equipment reform and technologies of one-step kiln process are primarily researched and applied into operation in China. Reduction behavior of two kinds of pellets using noncoking coal as reductant is studied and compared. The one is preheated pellet made of magnetite concentrate with composite binder, and the other is fired oxide pellets containing bentonite as binder [15]. Reducibility, compress strength, porosity, and microphases evolution are measured. Results show that preheated pellets possess much better reducibility than fired oxide pellets, which is ascribed to their higher effective diffusivity due to higher porosity. The compressive strength increases obviously after 30 min reduction and achieves a high value at the end of reduction, while the value of metalized pellets from reduction of oxidized pellets is much lower, because of more cracks and fractures formed. Xinjiang magnetite concentrate in China was studied by one-step process for direct reduction. The results show that for Xinjiang magnetite assaying with 69.21% Fe, damp milling and adding agent can improve the quality of green balls obviously. After drying, green balls are preheated at 800°C for 10 min, pellets with compressive strength of 581 N/pellet are achieved, preheated pellets were directly reduced at 1050°C for 80 min, and directly reduced iron assaying 90.33% of total iron and 85.05% of metallic iron and 94.15% of metallization degree are achieved. Compared with the traditional direct reduction of fired oxide pellets in coal-based rotary kilns, one-step process for direct reduction can avoid high-temperature oxidation of pellets at 1150–1300°C, and possess some advantages such as greater economic profit and good quality of direct reduced iron [28]. Weike one-step DRI plant with the annual output of 62,000 ton designed by Changsha Metallurgical Design and Research Institute in China started production in 2002, after more than 2 years trial test and technology renovation [29].

The FASTMET process, developed during the early 1990s by Midrex Direct Reduction Corporation to provide a coal-based process for North American locations, is very similar to the rotary hearth pioneered by Inmetco in Ellwood City,

Pennsylvania for treating waste dusts from steel plants and also a proposed process studied by Salem Furnace Company in Carnegie, Pennsylvania. The nucleus of the FASTMET process originated with the development of the heat fast process in the mid-1960s. The heat fast process consisted of the following steps: (1) mixing and pelletization of iron ore fines and pulverized coal, (2) drying the green pellets on a grate, (3) prereduction on an RHF, and (4) cooling in a shaft furnace. The next step in the evolution of the FASTMET process was the development of the Inmetco process for reduction of stainless steel mill wastes in 1974. The process consisted of the following steps: (1) mixing and pelletization of mill wastes and pulverized coal, (2) prereduction of the green pellets on an RHF, (3) discharge of hot pellets into transfer bins, and (4) charging of hot pellets into a submerged arc furnace. The process was tested in a pilot plant located at Port Colborne, Ontario, and a commercial unit of 60,000 tons per year capacity was set up in 1978 at Ellwood City, Pennsylvania.

Midrex revived investigations in 1989 and tested a wide range of raw materials in its laboratory in Charlotte, North Carolina. A 2.5 m (8.2 ft) diameter pilot RHF with a capacity of 150 kg/h of reduced iron was installed in 1991 to simulate the reduction portion of the process. This process simulator was utilized to develop data for the design of an industrial unit. Based on the successful laboratory and pilot plant tests, Midrex and its parent company Kobe Steel started construction of an FASTMET demonstration plant in April 1994 at the Kakogawa works of Kobe Steel in Japan. The plant has a production capacity of 2.6 tones/h and was commissioned in September 1995. The demonstration plant is reportedly operating under stable conditions, and several tests have been conducted to develop process parameters for scale-up to a 60 tone/h industrial scale unit. Tests have also been made for producing hot briquetted iron (HBI) and for integrating the FASTMET process with DRI melting in an electric arc furnace.

In the FASTMET process, shown schematically in **Figure 3**, iron ore concentrate, reductant, and binder are mixed and formed into green pellets that are dried at 120°C and fed to the rotary hearth furnace. The pellets are placed on a solid hearth one to two layers deep as shown in **Figure 4** [30–32].

As the hearth rotates, the pellets are heated to 1250–1350°C by means of fuel burners firing into the freeboard above the hearth. Reduction to metallic iron is completed in 6–12 min, depending on the materials, temperature, and other

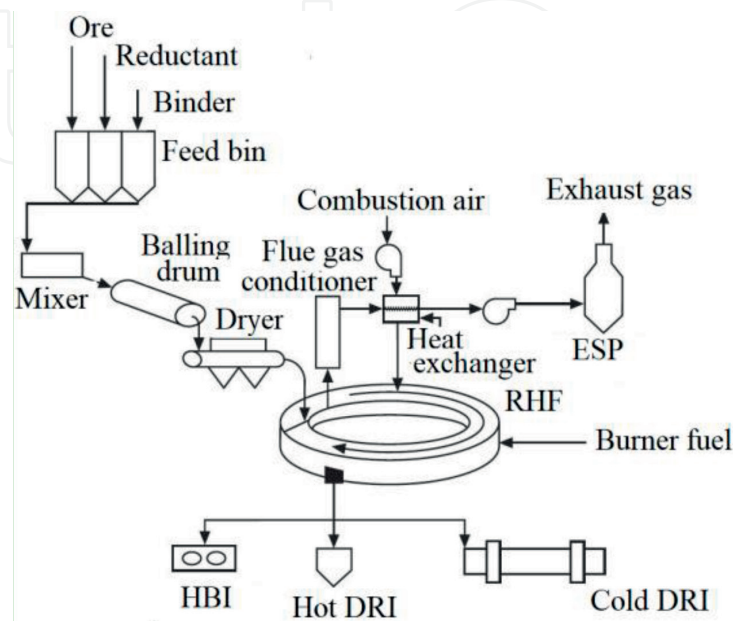


Figure 3.
Schematic flowsheet of FASTMET process [30].

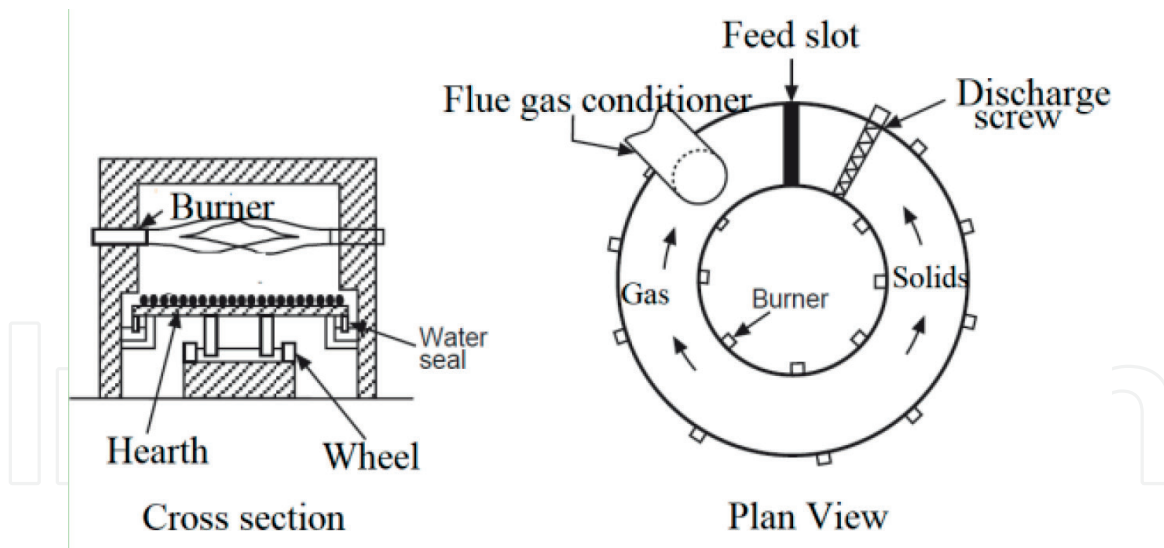


Figure 4.
Cross section and plan view of the rotary hearth furnace [30].

factors. The DRI is discharged at approximately 1000°C and can be hot charged to an adjacent melter, hot briquetted, or cooled indirectly before storage and/or shipment. The residence time of the pellets in the RHF is 12 min. The hot, reduced iron from the RHF is partially cooled to about 1000°C by a water-cooled discharge screw. The product can be obtained either in the form of cold DRI, hot DRI, or HBI. The product can be discharged from the RHF either to a transfer device for conveying the hot DRI directly to an adjacent steelmaking facility, or by gravity to a briquetting system for producing HBI. The off-gas from the RHF flows to a gas handling system, where the SO₂, NO_x, and particulates can be reduced to the desired limits. The hot off-gas is used for preheating the combustion air for the RHF burners and to supply the heat for drying. The process is designed to recycle all process water. All fines generated in the process are recycled through the feed.

3. Properties of pellets made from BOF wastes

General metallized pellet production processes are introduced above. In this section, the detailed properties of pellets made from BOF wastes, drying, and reduction behavior will be set forth further.

3.1 Generation and properties of BOF wastes

Converter sludge is a kind of black slurry with a high water content. It becomes a dense lump after dehydration and then dispersed into fine particles with large specific surface area after dispersion, among which the content of particle with a size below 0.075 mm is larger than 70%, while the percentage below 0.048 mm is larger than 50%. As the dust and mud are so fine that the surface activity is relatively large, it is easy to be absorbed and blown up into the air after drying, which seriously pollutes the surrounding environment. In terms of chemical composition, the total iron content is high and the impurity content is low. Most of them have simple composition, high content of iron ore, and relatively few impurities, which is conducive to comprehensive recovery and utilization. However, a strong alkaline hydroxide would like to be formed after absorbing water because of the contained CaO, MgO, K₂O, and Na₂O, which may lead to the increase of pH of the water and soil around and is bad for the growth of crops. Hence, reasonable recycling of BOF wastes is very important.

Item	TFe	FeO	CaO	MgO	SiO ₂	MnO	ZnO	Al ₂ O ₃	PbO	K ₂ O	Na ₂ O
wt, %	54.53	58.54	16.38	5.75	2.31	0.9	0.77	0.74	0.36	0.18	0.1

Table 1.
 Major chemical composition of converter sludge.

Chemical composition of the converter sludge obtained from a steelmaking company is shown in **Table 1**. Then, mineralogical phase was analyzed through the Laitz DMRX polarization microscope and the mineralogical content was characterized through X-ray diffraction (XRD) analysis.

3.2 Properties of pellets prepared from BOF sludge

To investigate the properties of pellets made from BOF sludge, the raw material was dried (at 105°C for 24 h in a drying oven) and finely ground with the size distribution listed in **Table 2**. Then, they were continuously charged into a pelletizing disk to prepare the green pellets. After that, the initial moisture content was obtained through drying method. In total, 100 g of green pellets were weighed and dried in the oven at 200°C for 24 h, and the difference of weights before and after drying was calculated as the moisture content. The compressive strength was measured according to the standard of ISO470016, and the falling strength (drop no.) was counted through repeated pellet falling from a height of 0.5 m to the steel plate with the thickness of 0.01 m until it cracked. In total, 10 balls were measured and the average was taken.

The bursting temperature was defined as the maximum temperature at which bursting rate was less than 4%. In total, 50 pellets were placed in a baking cup and heated for 3 min at the predetermined temperature with the flow rate of 1.5 m/s, then moved out, and observed. If two of them were cracked, the relative temperature was recorded as a bursting temperature.

Properties of green pellets were listed in **Table 3**. Moisture content was in the range of 15.29–16.78%, which was much higher compared to ordinary iron ore pellets (about 7–9%) [17, 18], and would make the drying more difficult. Pellets were strong enough with both high compressive strength and falling strength. However, the bursting temperature was low, so the temperature in the primary drying should be set as 150°C to avoid great bursting.

Figure 5 shows optical microstructures of the converter sludge. The major iron-bearing phases are magnetite (Fe₃O₄), iron, and wustite (Fe_{1-x}O) (**Figure 5a** and **b**). Some of hematite (Fe₂O₃) (**Figure 5a**) is also observed. Most of the iron-bearing phases are spherical, with the grain size smaller than 50 μm. Gangues observed are mainly composed of silicate crystal phase and glass phase, as shown in **Figure 5b** and **c**, and also coke particles are found in **Figure 5c** and **d**.

Size, mm	>0.5	0.5–0.3	0.3–0.15	0.15–0.105	0.105–0.076	<0.076
wt, %	36.74	8.46	11.24	1.33	14.33	27.90

Table 2.
 Size distribution of converter sludge after ground.

Item	Moisture (wt, %)	Compressive strength (N/p)	Falling strength (no. of drops/p)	Bursting temperature (°C)
Value	15.29–16.78	11.27–16.27	>20	150

Table 3.
 Properties of green pellets made from converter sludge.

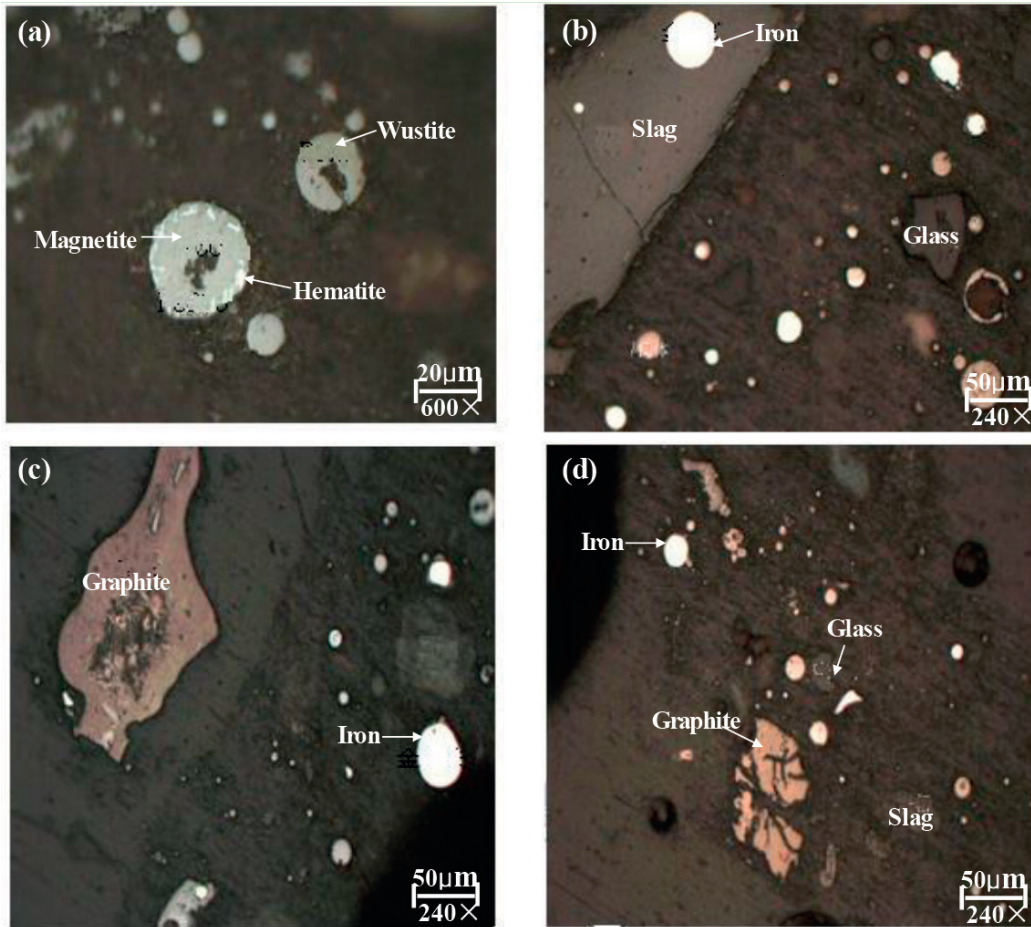


Figure 5. Optical microstructures of the converter sludge.

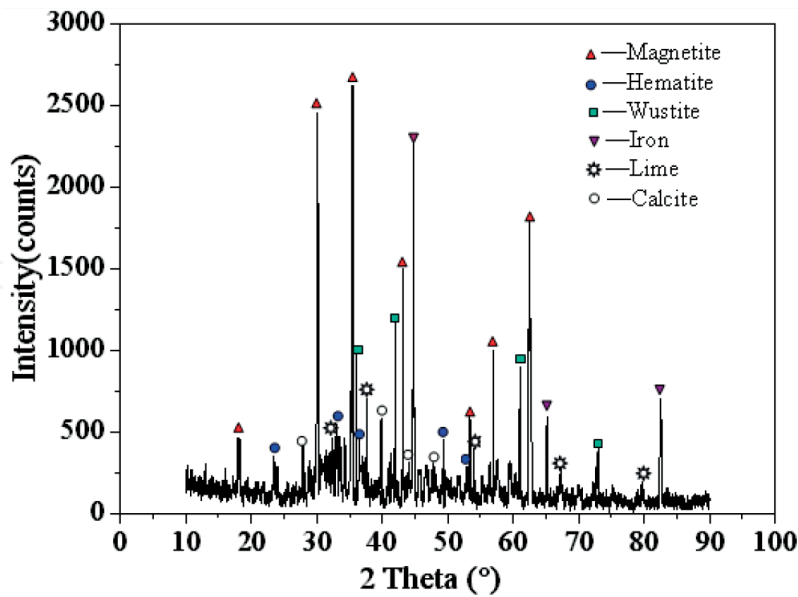


Figure 6. XRD analysis of the converter sludge.

This mineralogical composition of converter sludge is verified through XRD analysis shown in **Figure 6**. The particularly intense peaks of magnetite, iron, and wustite prove that they mainly comprise iron contained phase. The content of hematite is relatively lower. For the slag phases observed above, they are predominantly identified as CaO and CaCO₃.

The CaCO_3 is formed during the pelletizing with the reaction of formed slaking $\text{Ca}(\text{OH})_2$ and CO_2 in the air, and two positive charges of Ca^{2+} will produce strong electrostatic adsorption, which makes the green pellets strong enough [33]. However, so much lime in the sludge also brings the issue of much moisture content in the pellet (~16.52% in average) because of its high hydrophilic ability, which directly increases the risk of bursting during the drying.

4. Drying mechanism of BOF sludge pellets

Green pellets should be dried before being charged into the consequent preheating and reduction process or else they are easily to be cracked or pulverized owing to drastic volatilization of moisture at a high temperature, and this results in the significant drop of the permeability, which will eventually lower the metallization rate of the products in the reduction furnace, or even make the production abnormal. Additionally, it has been reported that about 25% of energy for pellet induration is consumed for drying [12]. Thus, the improvement of the drying performance will be energy efficient. The drying mechanism of iron ore pellets has been studied by several researchers [12, 34–36]. Two-stage drying is assumed for most drying models at first, involving surface evaporation and internal drying after a critical moisture content is reached [12]. Then, four-step drying kinetics of individual pellet is proposed and verified through experimental and numerical research by Tsukerman et al. [34]. Feng et al. investigate effects of some parameters on drying properties [35, 36].

Further research about drying characteristics of converter sludge pellets was studied to promote its recycle and reutilization [36]. Influence of factors including temperature, time, and flow on their drying properties were studied and optimized through experiments in order to get better reuse of secondary resources through the grate-kiln (or RHF) metalized pellet-producing process. Following is a brief introduction about the experiments.

In an actual production, drying in the traveling grate was divided into two stages [37]. This drying test was performed in the baking cup (with diameter of 80 mm and length of 300 mm) equipped with a crossflow adjusting system to simulate the two-stage thermal condition. The schematic was shown in **Figure 7**. Pellets are divided into three layers and placed in the baking cup (each layer with the height of 60–70 mm, and separated by a meshed stainless steel plate). Afterward, they were quickly covered by the burner and dried according to the scheduled time, flow, and temperature. Finally, they were moved out and cooled naturally. The bursting pellets for each layer were collected and weighed, respectively, and the remaining moisture was measured using the same method as the green pellets.

An orthogonal array was applied in this drying test. Four technical parameters were selected based on operation experience in pelletizing plant: first drying stage time (t_1 : 5, 7, 9 min), the second drying temperature (T_2 : 200, 300, 400°C), second drying time (t_2 : 2, 4, 6 min), and second drying flow rate (v_2 : 1.0, 1.4, 1.8 m/s, standard state), respectively. The temperature and flow rate in the first drying stage were set as fixed factors ($T_1 = 150^\circ\text{C}$; $v_1 = 1.5$ m/s) according to the previous bursting temperature measurement. Bursting rate of pellets and the dehydration rate were considered as two major indicators of drying characteristics and calculated according to the following equations.

$$\text{Busting rate (\%)} = m_1/m_0 \times 100 \quad (1)$$

$$\text{Dehydration rate (\%)} = (m_2 - m_3) / m_2 \times 100 \quad (2)$$

where, m_1 is the weight of bursting pellets, m_0 is the weight of total pellets, m_2 is the weight of water in green pellets, and m_3 is the weight of water in dried pellets.

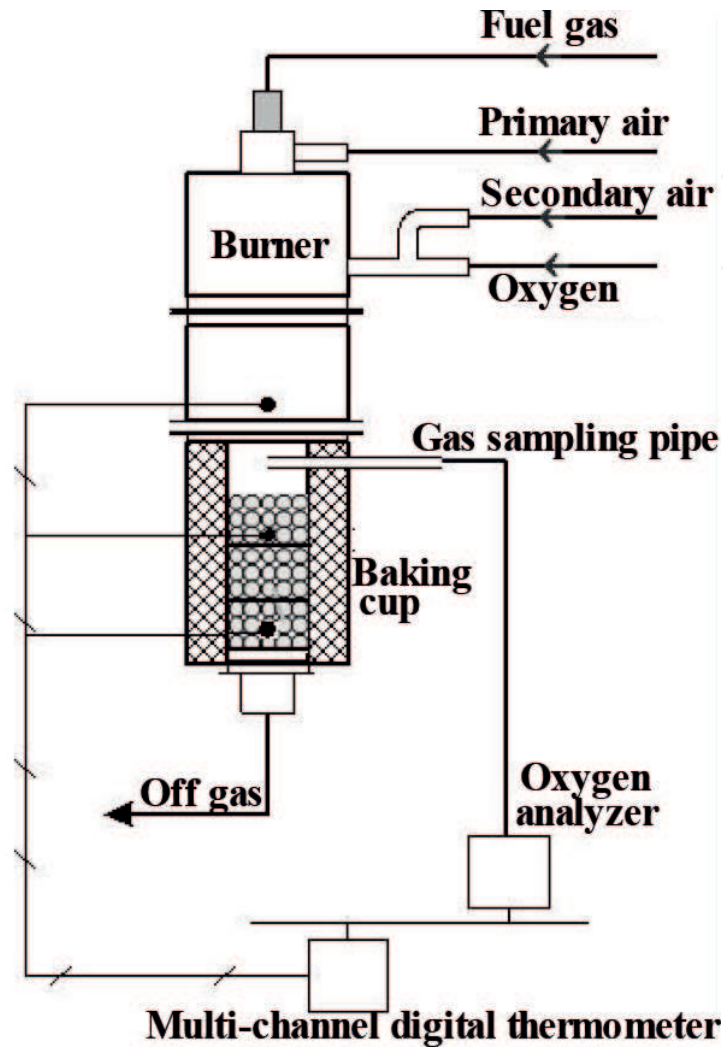


Figure 7. Schematic of the drying simulator.

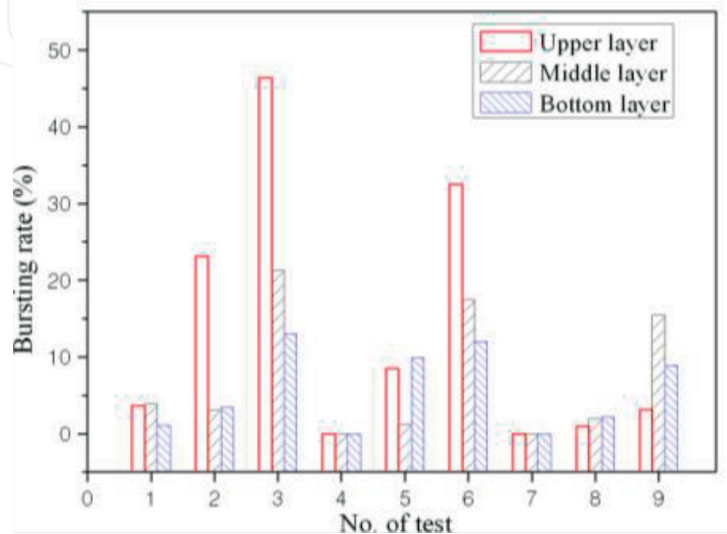


Figure 8. Bursting rate of dried pellets.

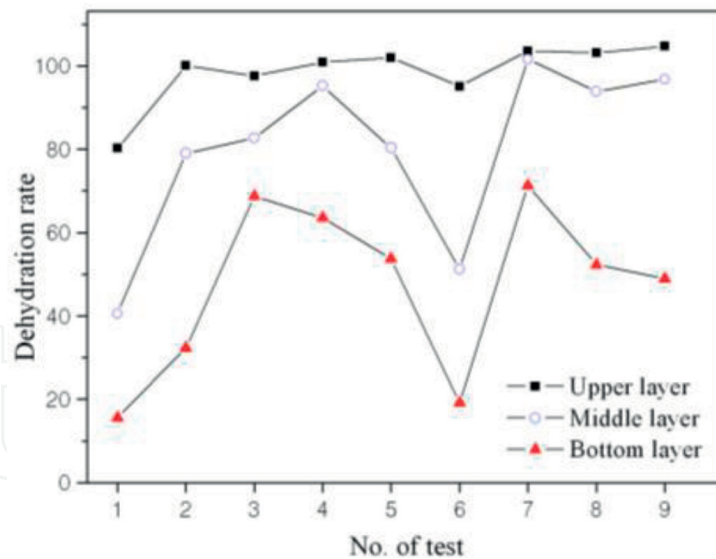


Figure 9.
Dehydration rate of dried pellets.

Figure 8 shows the bursting rate of pellets in each layer for the nine tests. High bursting rate means poor drying performance. It is found that bursting rate of the upper pellets in nos. 3, 6, and 2 is the worst, with the values of 46.41, 32.47, and 23.12%, respectively. Common conditions they share are short drying time (5–7 min) in first drying section, high level of temperature (300–400°C), and fast flow rate (1.4–1.8 m/s) in second drying section. It can be speculated that if the first drying time is not long enough, cracking rate of pellets will go up during the second drying section caused by the excessive expansion force generated through rapid and intense vaporization of residual moisture in the interior of pellet at high temperature and flow rate.

Figure 9 shows the dehydration rate of pellets in each layer. Obviously, the bottom pellets have the lower dehydration percentage compared with the upper and middle one, the lowest value of which are nos.1, 2, and 6, with 15.58, 32.31, and 19.16%, respectively.

Actually, moisture evaporation is a dynamic balance of liquid water gasification and vapor condensation, and evaporation rate is the difference of these two reactions [25]. It follows that the moisture evaporation velocity depends on the temperature and the pressure difference between saturated and ambient vapor. The higher the temperature and pressure difference, the faster is the evaporation rate. So, this is the reason why the dehydration rate in the bottom level is the lowest. For one thing, the temperature at the bottom is lower than the upper one as the endothermic evaporation reaction takes place when gas flows from up to down. For another, the vapor generated in the upper gradually enters into the main flow, which will lower the differential pressure of vapor.

5. Reduction mechanism of BOF sludge pellets

Most DRI production is melted in electric arc furnaces for steelmaking. Minor amounts may be charged into the ironmaking blast furnace. So the reduction degree, compressive strength, and dezincification rate are considered as three important indicators. They were energetically investigated by metallurgical researchers recently. The study of reduction behavior of the composite briquettes shows that both the metallization and dezincification ratios increased with the increasing temperature and the time, but first increased and then decreased with

the increasing C/O molar ratio [9]. The strength of the metallized pellet could be controlled by reduction temperature, sintering time, additive quality/quantity, and manner of reduction [22]. DRI strength values are found to decrease from 200 to 30 kg during reduction and then strengthened up to 50 kg as a result of sintering and fusion [23].

In order to clarify reduction mechanism of BOF sludge pellets, experiments to simulate the grate-kiln metalizing process is conducted. Flow diagram is shown in **Figure 10**, including converter sludge pellets preparing, drying, preheating in the baking cup, and subsequent direct reduction in the preheated pellets with reductant of coal in the simulated rotary kiln.

Experimental materials include the iron-bearing converter sludge and coal. Converter sludge's chemical composition and mineralogical phase are shown above. It mainly contains 54.53% TFe, 16.38% CaO, and 0.77% ZnO (weight percentage). The major iron-bearing phases are magnetite (Fe_3O_4), iron, and wustite ($Fe_{1-x}O$). Chemical analysis of coal as the reductant and its softening and melting

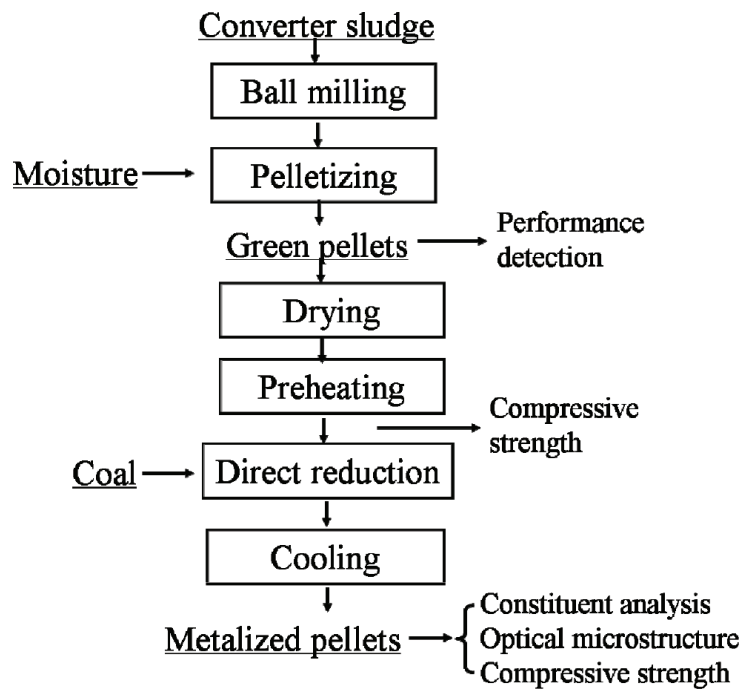


Figure 10.
Flow diagram of direct reduction experiment.

Composition	FC, ad	M, ad	A, ad	V, ad	V, daf
wt, %	76.18	0.72	9.68	13.42	14.98

ad = on air dry basis, daf = on dry ash free, FC = fixed carbon, M = moisture, A = ash, and V = volatile.

Table 4.
Chemical analysis of coal.

Item	Distortional temperature	Softening temperature	Half global temperature	Flowing temperature
Value, °C	1125	1180	1210	1280

Table 5.
Softening and melting properties of coal.

properties are shown in **Tables 4** and **5**, indicating it is suitable for direct reduction with high ash melting point.

The simulated rotary kiln is shown in **Figure 11**. It mainly consisted of a rotary drum (with a diameter of 130 mm and a length of 200 mm, made of heat-resistant steel) and an electrically heated tube furnace.

About 500 g of preheated pellets and coal at different ratio (C/O molar ratio) were put into the steel drum, which had been heated up to the target temperature in the furnace. Afterward, the direct reduction is proceeded for the predetermined residence time in the drum with a rotation speed of 30 rpm. Finally, they were moved out and cooled down to the ambient temperature. Optical microstructures of metallized pellets were analyzed through microscope. The compressive strengths before and after reduction were measured. Metallization rate was calculated on basis of chemical analysis according to the following equations.

$$\text{Metallization rate (\%)} = \text{MFe(\%)} / \text{TFe(\%)} \times 100 \quad (3)$$

where, MFe means metallic iron, and TFe means total iron.

Nine tests were conducted, and three technical parameters including temperature (1000, 1050, and 1100°C), time (1.5, 2.0, 2.5 h), and coal ratio (C/O molar ratio, 1.1, 1.3, and 1.5) were selected. Results show that the nos. 3 (T = 1050°C; t = 2.5 h; C/O = 1.5), 2 (T = 1050°C; t = 2 h; C/O = 1.3), and 6 tests (T = 1100°C; t = 2.5 h; C/O = 1.1) have the highest metallization rate of 74.7, 47.7, 45.7%, respectively. Common conditions they share are relatively long reaction time and high reduction temperature. Their corresponding compressive strengths are 1014, 897.4 and 1506.7 N/p, indicating pellets produced from certain tests meet the strength requirement of material served for BF. In addition, the residual zinc contents of these three reduced pellets are 0.44, 0.54, and 0.38%, and the average dezincification rate is calculated as 41.6%. This index can be further improved in an actual rotary kiln because the vapor of zinc produced during reduction could be brought out with the flow.

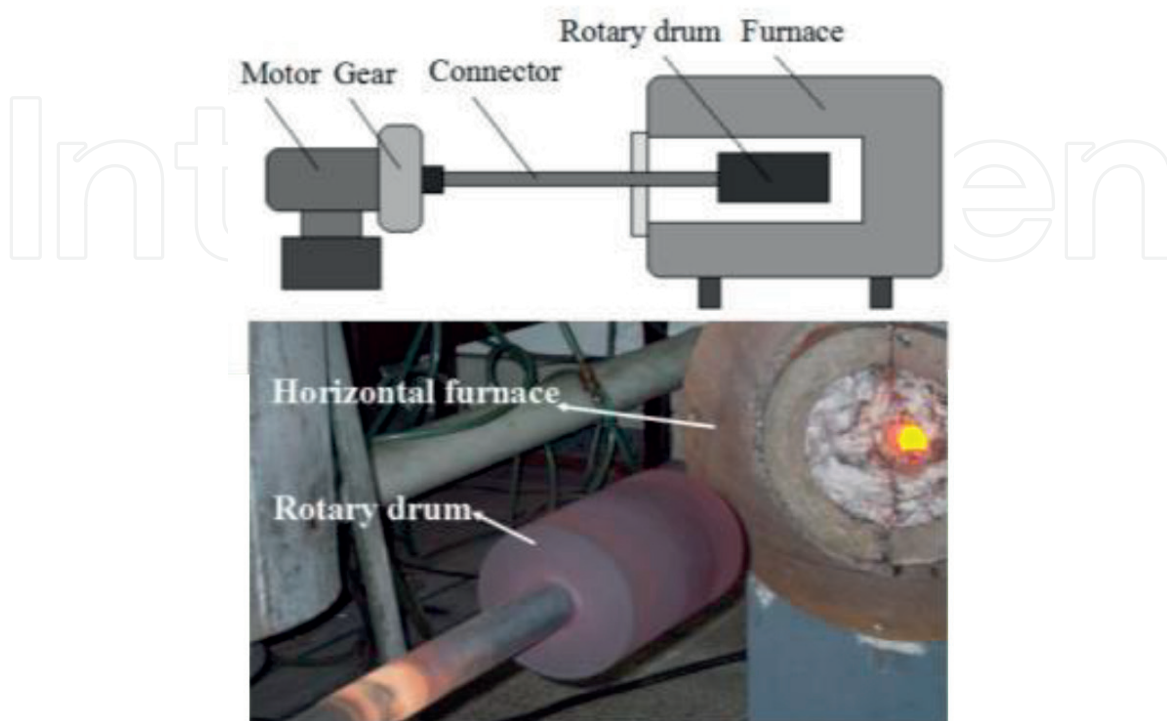


Figure 11.
Schematic of the metalizing simulator.

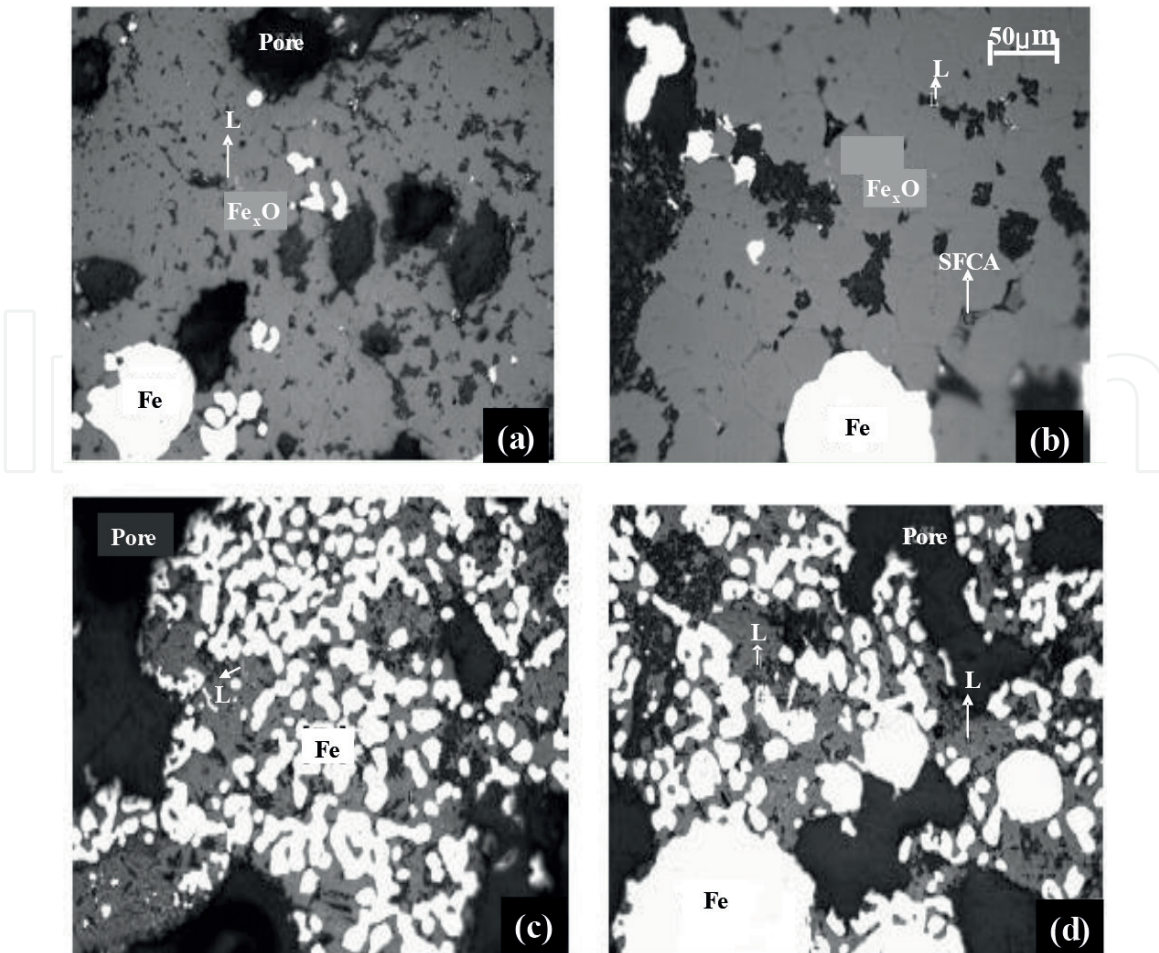


Figure 12. Optical reflecting microstructures of the reduced pellets, 200 \times : (a) and (b) interior and (c) and (d) exterior. L: silicate, SFCA: composite calcium ferrite, Fe: metallic iron, and Fe_xO : wustite.

Figure 12 shows optical microstructures of the reduced pellets. A lot of wustite exists in the interior of metalized pellets as shown in **Figure 12a** and **b**, while a large amount of metallic iron, which looks much whiter and brighter than wustite, is mainly observed in the exterior shown in **Figure 12c** and **d**. It can be deduced that the reduction condition in the out part of pellets is much better than the interior at the beginning, and the compact shell of iron rapidly formed in the initial makes the diffusion of reduction gas more difficult from outside to the inner.

6. Conclusions

Converter sludge is a kind of useful secondary resource rich in valuable iron and calcium oxide. High initial moisture in converter sludge enhanced the bursting risk during drying and made this process difficult. The upper layer bursting rate and the bottom layer dehydration rate are considered as main indicators of drying performance. Technical factors of temperature and retention time in the drying section have remarkable influence on the drying performance, which should be paid close attention in future.

Two-step and one-step coal-based methods have been extensively researched recently and adopted into operation of the BOF wastes recycling. Effects of direct reduction parameters including temperature, time, and coal ratio on the metallization rate and compressive strength are also studied. Results show that reduction time and temperature have remarkable influence on the metallization rate. The

indexes of metallization rate and compressive strength of metallized pellets reduced from the BOF sludge can satisfy the requirement of iron burden for BF. To improve the efficiency, the gas-based direct reduction especially hydrogen as the reductants may be considered to develop breakthrough technologies for emission reduction.

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Conflict of interest

There is no conflict of interest.

Other declarations

Mutual development of metallurgical technology and ecological environment is our persistent pursuit.

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