Effect of Nut Coke on the Performance of the Ironmaking Blast Furnace

PhD thesis July 2013

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Effect of Nut Coke on the Performance of the Ironmaking Blast Furnace

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To my family...

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1. INTRODUCTION

1.1 Project background

Steel is one of the most attractive, most robust and most sustainable materials in the world [1]. It is the material that could be designed for and innovated in many aspects of our lives, for example in vehicles, buildings, mechanical equipment, maritime applications, medical devices, household equipment and so on. Steel is also a 100 % recyclable material. Therefore, it contributes significantly to the long-term conservation of resources fundamental for future generations. In the current trend, the ironmaking blast furnace and oxygen steelmaking route still remains the primary source for worldwide steel production. The modern blast furnace has advanced with large steps from its earlier ancestors. Most modern large-capacity blast furnaces represent extremely efficient chemical reactors, capable of stable operation with an impressive range of reactant feed materials.



Figure 1-1 Ironmaking and oxygen steelmaking process [2]

Figure 1-1 shows the typical route for the ironmaking and oxygen steelmaking process. A blast furnace uses coke and coal as the main reductant sources and iron ore (sinter, pellet and lump ore) as the iron-bearing component together with

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limestone to produce hot metal. Since the blast furnace produces hot metal that is saturated with carbon (from the coke), the targets of steelmaking in the basic oxygen furnace are removing of carbon and other residual impurities (e.g., phosphorus, sulphur) [3]. The steel refining process in the ladle consists of further purifying the hot metal, adjusting and homogenizing the chemical properties and temperature of the metal. The final refining adjusts the steel to the required characteristics for the next step of continuous casting into slabs, blooms or billets. These semi-products will be further processed in rolling mills.

The increase in global steel production caused a pronounced spike in prices for raw materials in recent years [1]. Therefore, nowadays the blast furnace process highly needs to be further developed. This can be incremental or through entirely novel technology improvements that are more efficient, more productive, consume less resource, and generate less environmental pollution. The blast furnace consumes a large amount of high quality metallurgy coke (size 40-80 mm) every year; however, small size (nut) coke is rarely used. Therefore, a large fraction of coke is not used for reduction. Recent research pointed out that usage of nut coke will be economical if properly used. Nut coke can't be directly mixed with normal coke because it will decrease the permeability of the coke layer in the blast furnace. However, mixing nut coke into the ferrous burden layer is an effective way to use the coke resource economically. This way could improve softening and melting behaviour, reduction kinetics and permeability and also make full use of the coke resource. It may, however, also worsen the layer permeability and even cause vital damage to the whole blast furnace process. The mechanism of the effect of nut coke on the performance of the blast furnace is still not clear. Therefore, the usage of nut coke is still limited.

What is nut coke? There is no clear definition of nut coke grain size. It is normally defined as the coke size smaller than 40 mm in industry. Figure 1-2 shows a typical size distribution of coke produced from a coke oven. It can be seen that the proportion of size smaller than 40 mm is around 20 %. In the traditional view, almost 20 % production of the coke oven can't be directly used in the blast furnace. To obtain the required size and amount of coke, the process of coke making demands costly efforts to control pollution to the environment [2]. The coke making process generates particulate matter (PM), volatile organic compounds (VOCs), polynuclear aromatic hydrocarbons (PAHs), methane, ammonia, carbon monoxide, hydrogen sulphide, hydrogen cyanide, and sulphur oxides, Coal charging, coke pushing, and quenching are potential sources of dust emissions [3].



Figure 1-2 Distribution of coke size [4]

From above discussions, it can be seen that the usage of nut coke is very significant both for improving blast furnace performance and protecting the environment. This urges the need to make maximum use of the coke resource.

1.2 Overview of blast furnace ironmaking

Figure 1-3 shows an overview of the modern blast furnace system. The blast furnace is a very complicated, smart and giant system. The oldest extant blast furnaces were built during the Han Dynasty of China in the 1st century BC. It has evolved around many years to become an efficient and intelligent counter-current exchanger of heat and counter-current exchanger of mass.

This complicated system includes the following important parts [5]:

- Hot blast stoves: Air is preheated to temperatures between 1000 °C and 1250 °C in the hot blast stoves. The hot air is delivered to the blast furnace via a hot blast main, bustle pipe, tuyere stocks and finally through the tuyere. Tuyere is a set-up for hot gas going to the blast furnace raceway.
- Stock house: The burden materials (iron sources) and coke are delivered to a stock house. The materials are screened and then weighted before final delivery into the furnace. The burden materials and coke are brought to the top of the furnace via skips or via a conveyor belt, where they are discharged into the furnace in separate layers of ore and coke.

- Gas cleaning: The top gas leaves the furnace via uptakes and a downcomer. The top gas may contain many fine particles and so to remove as many of these as possible the top gas is lead through a dust catcher and wet cleaning system.
- Casthouse: The liquid iron and slag collect in the hearth of the furnace, from where they are tapped through the taphole via runners in the casthouse into transport ladles.
- Slag granulation: The slag may be quenched with water to form granulated slag, which is used for cement manufacturing.



Figure 1-3 Overview of a modern blast furnace system [5]

The blast furnace is a counter-current heat and mass exchanger, heat is transferred from gas to burden and oxygen from burden to gas. Gas ascends up the furnace while burden and coke descend down through the furnace. The counter current nature of the reactions makes the overall process an extremely efficient one [6]. A blast furnace is filled with alternating layers of coke and the iron ore-containing burden as shown in Figure 1-4. Hot blast is blown into the blast furnace via tuyeres. In this process, the oxygen in the blast furnace is transformed into gaseous carbon monoxide. The resulting gas has a high flame temperature between 2100 °C and 2300 °C. Coke in front of the tuyeres is consumed thus creating voidage. The very hot gas ascends through the furnace, carrying out a number of vital functions, such as heating up the coke in the bosh/belly area and materials in the shaft zone, melting the iron ore in the burden and creating voidage. Upon melting, the iron ore produces hot metal and slag, which drip down through

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the coke zone to the hearth, from which they are removed by casting through the taphole. In the dripping zone the hot metal and slag consume coke, creating voidage. Additional coke is consumed for final reduction of iron oxide and carbon dissolves into the hot metal, which is called carburization.





1.3 Some aspects of blast furnace performance

1.3.1 Permeability

Permeability is one of the most important issues to maintain a smooth blast furnace performance. A bigger permeability index indicates a better permeability. The permeability index ζ is defined as:

$$\zeta = \frac{V_{blast}}{\Delta p} \tag{1-1}$$

where,

 V_{blast} : Blast volume, m^3/min Δp : Pressure drop of whole stock column, Pa

Permeability is a parameter controlled by blast volume and pressure drop of the stack column. Under the constant condition of blast volume, the permeability could be improved by decreasing the pressure drop. The Ergun equation is a classical formula for calculating the pressure drop of the packed bed:

$$\frac{\Delta p}{L} = 150 \frac{\eta U (1-\varepsilon)^2}{(d_e \phi)^2 \varepsilon^3} + 1.75 \frac{\rho_g U^2 (1-\varepsilon)}{\phi d_e \varepsilon^3}$$
(1-2)

where,

Viscosity of gas, $Pa \cdot s$ η 1 U 1 Velocity of gas, m/sε Porosity of packed bed 1 : Equivalent diameter, m d_{ρ} Shape factor : φ Pressure drop of unit length packed bed, Pa/m $\Delta p/L$ •

The condition of the stack column is different in different zones of the blast furnace and thus the pressure drop should be discussed individually for different zones. In the blast furnace, a higher porosity and a bigger particle size will lead to a lower pressure drop and the lower pressure drop will bring a better permeability under a constant blast volume based on equation (1-1).

In the lumpy zone

The lumpy zone is the zone of the stack where no softening phenomenon takes place. All the particles keep almost their original shape. In the lumpy zone, the permeability is mainly determined by the porosity and particle size. If there are too many fines, the porosity of the packed bed will reduce which could affect the bulk gas flow through the burden layer. Part of the fines is generated in the descending process due to the friction, collision and thermal expansion of particles. The other sources of the fines are directly charged small size ore or coke particles. Generally speaking, the size below 5 mm is defined as fine particles. When the size is smaller than 5 mm, the resistance of gas through the packed bed is obviously enhanced. When the size is bigger than 25 mm, the gas resistance of the packed bed keeps almost constant. It indicates that the ore particle size between 5~25mm fits the blast furnace performance [7].

As the ideal condition, the porosity is not related with particle size. But in industrial practice, the porosity is influenced by the size ratio as well as the fraction of different size particles. It can be seen from Figure 1-5. It demonstrates that the porosity decreases greatly as the ratio d_s/d_l decreases. d_s is the diameter of small size particle and the d_l is the diameter of big size particle. It means that in order to obtain a good permeability, the size fractions should be as narrow as possible in a mixed bed [8].



Figure 1-5 The relation of porosity with size ratio and fraction of big size particle [8]

In the cohesive zone

Liquid phases (molten iron and slag) are generated and drip to the hearth through the void of coke layer in the cohesive zone. Since these liquids reduce the free cross-section available for the flow of gases, the pressure drop increases with the increased fraction of liquids. Thus, the pressure drop in the cohesive zone is much higher than in the lumpy zone due to the melting slag and iron filling the voids of the coke layer, and also due to the deformation of iron ore particles. If the resistance for gas flow is too high, it will result in holds-up or flooding. Gases not only flow through the voids of coke but also through the liquid phased holds-up in the voids. It makes fluid dynamics parameters rather complex. The slag property is also a very important factor for improving the permeability of the cohesive zone. Lower viscosity and lower amount of slag are beneficial for a higher permeability. In the cohesive zone, gas flow mainly depends on the voids of the coke layer and on slag properties. Thus, enhancing the coke strength and improving the size range and slag properties are very significant for improved blast furnace permeability.

1.3.2 Reduction behaviour

Iron oxide contained in the iron ore is the key substance for the ironmaking blast furnace. The process for extraction of iron from iron oxide is the basic and the most important target for the blast furnace reactor.

Scientific research and industrial practice have proven that the reduction of iron oxide is stepwise from higher oxide to lower oxide, no matter which kind of reducing agent is applied.



Figure 1-6 Schematic view of the iron ore reduction process [6]

The reduction process is best illustrated in Figure 1-6 for iron oxides particles. Starting with a dense sphere of hematite Fe_2O_3 (similar to pellets), an initial reduction with CO or H_2 will produce a shell or layer of metallic iron in contact with wüstite, FeO. Inward from the wűstite there will be a layer of magnetite Fe_3O_4 surrounding the core of hematite. The chemical part of the reduction reaction of iron ore can be split into two or three distinct phase transitions depending on temperature. Below 570 °C hematite reduces to iron with magnetite as intermediate phase. Above 570 °C hematite is reduced to magnetite and subsequently to wüstite before all oxygen is removed and iron is formed.

When
$$T < 570$$
 °C

$$3Fe_2O_3 + CO(H_2) = 2Fe_3O_4 + CO_2(H_2O)$$
(1-3)

$$0.25Fe_3O_4 + CO(H_2) = 0.75Fe + CO_2(H_2O)$$
(1-4)

When T > 570 °C

$$3Fe_2O_3 + CO(H_2) = 2Fe_3O_4 + CO_2(H_2O)$$
(1-5)

$$\frac{w}{4w-3}Fe_3O_4 + CO(H_2) = \frac{3}{4w-3}Fe_wO + CO_2(H_2O)$$
(1-6)

$$Fe_w O + CO(H_2) = wFe + CO_2(H_2O)$$
(1-7)

Ironmaking in the blast furnace is a very complicated process under multi-phases and fluid flow conditions. The reduction reaction of iron oxide is studied from thermodynamics and metallurgical kinetics. Thermodynamics is used to determine the possibility, the direction and the limit of the reactions. It only considers the beginning and final status of the thermodynamic system. Metallurgical kinetics mainly focuses on the reaction rate and the reaction mechanism and finds out the restrictive step. It not only focuses on the beginning and the end but also on the time line of the reaction. As most metallurgical reactions are conducted under multi-phases and high temperature conditions, reaction rates are relatively high

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compared with diffusion and mass momentum transfer. Most metallurgical reactions, for instance reduction of iron oxide, are controlled by diffusion and mass transfer. The ironmaking process is accompanied by fluid flow and heat transfer. Therefore momentum transfer, heat transfer and mass transfer should be deeply investigated to establish the reduction reaction of iron oxide.

The Fe-O phase diagram is the theoretical basis for analysing the reduction process of iron oxide. It can be seen from Figure 1-7 that with the increase of the percentage oxygen, the transition order is $Fe \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$ below 570 °C. It is $Fe \rightarrow Fe_xO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$ when the temperature is higher than 570 °C. It indicates that wustite is only stable above 570 °C. When the temperature is lower than 570 °C, it decomposes into *Fe* and *Fe*₃*O*₄:

$$4FeO(s) = Fe_3O_4 + Fe$$
 (1-8)



Figure 1-7 Fe-O phase diagram [8]

For the reduction reactions of iron ore by the reducing gasses CO and H_2 in equations [1-3] to [1-7], equilibrium diagrams can be constructed. In the equilibrium diagram, the stability of the different iron oxide phases at different gas compositions and temperatures is shown (see Figure 1-8). In the blast furnace the reducing gas consists predominately of CO with varying amounts of H_2 . In the diagram the gas composition of CO and CO₂ (or H_2 and H_2 O) is expressed as the

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faction of CO (or H_2) in the reducing gas atmosphere. For the Fe-O-CO equilibrium, the diagram is divided into three zones by three curves, which are named Fe_3O_4 , FeO and Fe stable zone. When the concentration of CO is higher than the equilibrium concentration under a certain temperature of one curve, the reaction of this curve could proceed as the equations [1-3] to [1-7] from left to right.

To compare the reduction characteristics of CO and H₂, the Fe-O-H₂ system is also shown in Figure 1-8. Both curves of reduction of Fe₃O₄ and FeO with CO and H₂ as the reducing agents intersect at 821 °C. These curves always go down when H₂ acts as the reducing agent. It indicates that H₂ is a powerful reducing agent at high temperatures. Especially when the temperature is higher than 821 °C, the reducing ability of H₂ is higher than that of CO.



Figure 1-8 Fe-O-CO and Fe-O-H₂ equilibrium diagram [8]

The Boudouard reaction (1-9) is a very important issue which influences the reduction of iron oxide.

$$C(s) + CO_2(g) = 2CO(g)$$
(1-9)

Theoretically the Boudouard reaction has its maximum instability between 600 $^{\circ}$ C and 800 $^{\circ}$ C, however in practice the reaction starts at a higher temperature. The CO gas provided by the Boudouard reaction is used for the reduction of iron oxides. The interaction between the Boudouard reaction and the reduction of iron oxide by CO is referred to as direct reduction. The direct reduction reaction (1-10) for wüstite is found when combining reaction (1-7) with (1-9):

$$FeO(s) + C(s) = Fe(s) + CO(g)$$
 (1-10)

The Boudouard reaction is highly endothermic and the ΔH_{298}^{θ} =165390 J/mol, and is therefore energy consuming. However, the direct reduction consumes less carbon than the indirect reduction for every mole of oxygen removed. In Figure 1-9 the stability diagram of the Boudouard reaction is shown. At high temperatures CO₂ is unstable and will decompose into CO in the presence of carbon. The reverse reaction is called carbon deposition [7].



Figure 1-9 The stability diagram of CO and CO₂ in presence of carbon at various temperatures and the influence of total pressure [8]

1.3.3 Softening and melting phenomenon

The softening temperature is defined as the temperature where the metallic iron shell around an iron ore particle cannot hold the load of the overlying burden any longer. At that moment, iron ore particles become deformed and contract. During the softening process, iron ore is further reduced and heated by the hot reducing gas and then it starts to melt. When the molten slag and metallic iron accumulate to a certain amount, they will drip down to the hearth. The temperature at which this happens is defined as the dripping temperature. The melting temperature is divided into melting onset temperature and complete meltdown temperature. The difference between softening temperature and melting temperature is defined as

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softening and melting range. A narrow softening and melting range (higher softening temperature and lower melting temperature) implies better softening and melting properties. Because it leads to a thin cohesive layer and it is beneficial for gas flow through the thin layer.

It is known that the metallic burden reaches the softening temperature with a reduction degree higher than 50 % [9]. Based on the shrinking core reduction mechanism of iron ore, it can be assumed that there is a porous solid iron shell surrounding the solid iron oxide and liquid slag layer [10] as shown in Figure 1-10. The remaining solid iron oxide is covered by the liquid phase which acts as a lubricant. The core of iron ore has a very low mechanical strength after the liquid wets all the remaining solid iron oxide. Thus the resistance to deformation of the whole particle should be determined by the metallic iron shell [11]. It can be seen that the metallic shell and the properties of the liquid phase are critical factors for softening and melting behaviour.



Figure 1-10 Schematic view of partial reduction of iron ore

The shell of metallic iron plays an important role with respect to the mechanical strength of the single iron ore particle. The strength of the metallic shell is determined by the thickness of the shell and the composition of metallic iron, i.e. carburization. The thickness of the metallic shell is correlated to the reduction degree. The thickness grows when the reduction degree increases. High reduction degree will cause high strength of metallic shell [11]. However, the composition of the metallic iron is also a key issue for the shell strength. With increasing carburization, the melting point of the iron-carbon alloy goes down which is shown in the Fe-C phase diagram (Figure 1-11). It means that high carburization lowers the strength of metallic shell. Carburization will coarsen the structure of the iron shell and will lead to the formation of cracks in the iron shell.



Figure 1-11 Fe-C phase diagram [12]

Slag mainly contains SiO₂, AI_2O_3 , CaO and MgO [8]. The chemistry, distribution and morphology of the slag influence the melting point, viscosity and basicity of the liquid phase. It will indirectly influence the mechanical strength of the iron ore particle. The liquid phase surrounds the remaining oxide particles in the core and tends to wet the oxide particles. With increasing temperature the viscosity decreases while the liquid fraction increases which in turn increases the pressure on the metallic shell. It lowers the mechanical strength to withstand the load of overlying ferrous burden and coke [11]. As the liquid oxide volume fraction increases, it will tend to move from the oxide core to the metallic shell generating a macro-porosity in the oxide core [10]. Surface energy and viscosity are the key points for the transporting procedure.

1.4 Objective and structure of the thesis

Industrial practice of mixed charging and adding nut coke in the burden layer of blast furnaces has been introduced in some countries. Operation of blast furnaces proved the possibility of coke saving and increase of furnace efficiency when adding nut coke into the burden. However, the mechanism of this phenomenon and consequently the limit for nut coke consumption, are still not completely clear. In particular, reduction kinetics, softening and melting and permeability have not been studied deeply enough. Current theories are unable to accurately account for the behaviour of the cohesive zone when using nut-coke mixed with ferrous materials. Therefore, more comprehensive understanding in relation to the effect of mixing degree of coke and ferrous material in blast furnaces is required. The objective of the thesis study is to gain an in-depth understanding of the reduction mechanism, softening and melting behaviour, the porosity/permeability change and pressure drop in the burden and cohesive layers, when adding nut coke into the ore layer. It aims to find out the optimum nut coke mixing ratio and the effect of nut coke size on the blast furnace performance. The outcome will provide further knowledge on the thermodynamic limits and reaction rate of iron ore reduction, in relation to the use of nut coke in the ferrous burden materials.

Both the cold flow model and high temperature experiment were adopted in this thesis. The cold flow model was conducted to investigate the effect of nut coke on permeability in the "dry zone" of the blast furnace. The high temperature experiment aims to study the reduction, softening and melting and also permeability in the "wet zone" of the blast furnace. Pressure drop was measured to evaluate the permeability and the contraction of the sample bed was recorded to determine the softening and melting temperature. The off-gas was online analysed to calculate the reduction degree and providing information for kinetics analysis. XRF, XRD and SEM-EDS-BSE technologies were applied to analysis the sample before and after experiment.

The contents of the chapters are summarized as follows.

In Chapter 2 an overview of published literature about usage of nut coke in recent years is given. It demonstrates the study approach used this field.

In Chapter 3, in order to know the effect of nut coke on the permeability in the blast furnace "dry zone", a cold flow model is established. Different nut coke size, nut coke mixing ratio and also different numbers of layers are tested. A CT scanner is used to obtain the inner information of the packed sample bed. Finally, a three layers permeability model is established.

In Chapter 4, the high temperature experiment is described. Facility, research plan, analytical method and data interpretation are introduced.

In Chapter 5, it shows the results of high temperature experiments. The effect of adding nut coke in ferrous burden on reduction, softening and melting and permeability is discussed. The mechanism of nut coke consumption is also studied.

At last, the main outcome of this thesis research is finally presented as conclusions and summary.

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2. LITERATURE REVIEW

Coke plays a key role in blast furnace performance and constitutes a great portion of the production cost of hot metal. Therefore, study of coke saving and blast furnace efficiency improvement have attracted many researchers. Yang and Yang have shown that proper mixing of coke with ore improves blast furnace operation [1]. They investigated the effect of coke-ore mixed charging through laboratory experiments with different ratios of mixed coke. They pointed out that mixed charging improves the permeability of the softening and melting (SM) layer, especially direct reduction. For smaller sizes of coke (nut coke) a superior effect will be expected. In recent years there have been increased interests in using nut coke in the blast furnace [2]. The interest comes from the possibility of reducing unproductive losses of coke ovens, optimizing the gas dynamic regime of the smelting operation, and improving its main techno-economic indices by adding nut coke into the ferrous burden layer. In the past years, usage of nut coke was different from 10 to 20 kg to 70~100 kg per tonne hot metal (tHM) in Europe, Japan and elsewhere [3].

As illustrated above, the effects of nut coke and ore mixing on gas permeability and high temperature properties are worth of further investigation considering the mixed coke size, mixing degree and layer thickness when attempting industrial application. However, the coke/ore mixing ratio in large blast furnaces continues to be limited.

This chapter will demonstrate the state of art of using nut coke in ferrous burden and also show a review of cold flow model and high temperature experimental facilities adopted previously for studying the performance of the blast furnace on laboratory scale.

2.1 Effect of mixing nut coke to ferrous burden

2.1.1 Permeability

Permeability is one of most important factors in blast furnace operation, because permeability determines how the reducing gas flows through the furnace. The way it flows will influence the productivity. Many investigators [2, 4-9] believe that the pressure drop can be decreased by adding the coke and/or nut coke into the ferrous burden (mixed charging).

Makhanek et al. [10] tested with large pieces of coke (40 mm) and small pieces of coke (25~40 mm) during two periods in an industrial blast furnace. The first period was operated with 100 % large pieces (>40 mm). The second period was operated

with a mixture of 50 % large and 50 % small pieces (25~40 mm). Keeping the same ore amount during both periods, they found out that the pressure jump of furnace gas increased and varied with the amount of small size of coke. The operation of the furnace was more even with increasing percentage of the small size coke. They pointed out that the main reason for the higher output is the reduced expenditure of coke. The heating and reducing capacity of the gas flow is completely utilised due to the better distribution of the gas and the more even operation of the furnace.

Kokubu et al. [11] found out that H₂ can decrease the pressure drop of a sinter bed under load test. They concluded that H₂ addition (CO based, H2: 0 %~8.4 %) can improve the resistance of the sample burden and changes the beginning temperature of pressure drop to a higher temperature. Figure 2-1 is the pressure drop changing with different H₂ content. It can be clearly seen that the pressure drop decreases when H₂ changes from 0~8.4 %.



Figure 2-1 Change of testing curves with H₂ in case of self-fluxed sinter [11]

Okuda et al. [12] investigated the blast furnace operation using a large amount of small size coke (7~20 mm) mixed with ore. They pointed out the weight of small size coke is 12~17 kg/THM usually. The weight they tested is 28Kg/tHM at Kimitsu No. 2 blast furnace. They concluded that mixing of small size coke into the ore layer prevented the permeability deterioration in the lower part of the blast furnace. They guessed that the lump normal coke remains large in the lower part as the result of selective solution loss reaction of small size coke. The permeability of the cohesive layer is good as a result of mixing of small size coke with ore.

Hotta et al. [13] studied the mixed layer properties of ore and coke. Two methods for mixing layers are shown in Figure 2-2. The first one is changing height and number of layers (2-5 layers). The second one is changing the mixing degree of coke into the ore layer (mixed layer).



Figure 2-2 Various conditions of mixing of ore and coke [13]

They found out that the pressure drop decreased with the decrease of layer height (increase of layer number) and the peak disappeared under the conditions of more than 3 layers. The pressure drop became lower rapidly with increase of the weight of mixed coke and the peak disappeared in the case of more than 6.4 wt% (90 g) shown in Figure 2-3 and 2-4. They thought that carburization occurred at the interface of the sinter and coke. When metal melting at the boundary, gas mainly passes through coke and its surroundings and the permeability of the packed layer is maintained enough.



SAMPLE:SR+CK WEIGHT OF COKE SR AMD CK [309] ST AMD CK [309] SR AMD CK [209] SR AMD CK [200] SR AMD CK [

600

Figure 2-3 Effect of layer number on pressure drop [13]

Figure 2-4 Effect of coke weight on pressure drop [13]

Generally speaking, the bigger the voidage in the burden layer, the higher the permeability will be. However, through a gas dynamics experiment, Du et al. [4]

found that when small size coke is mixed in the burden layer, voidage decreased, but the permeability improved compared with normal charging. They pointed out that both the voidage and the voidage structure should be considered when studying burden permeability [4]. Through blast furnace test, they said that the coke rate decreased 18.89 kg/THM and production increased 6.3 % when adding coke into the burden layer. Mixing rates changed from 20 %-100 % and coke size consisted of 10-25 mm, 25~40 mm and 40~60 mm.

Isobe et al. [14] found that mixing nut coke (8~11 mm) into the ore layer can reduce the gas resistance of the cohesive zone on laboratory scale. They tested two charging conditions of the sample shown in Figure 2-5. In case A, with an increase of mixing nut coke degree (1, 3, 5, 7 wt%), the temperature range showing the high pressure drop area was narrowed, and the maximum pressure drop was reduced (Figure 2-6). The same phenomenon appears in case B with coke contents of over 3 wt%. However, when the coke content under 3 wt%, there is a difference between A and B as shown in Figure 2-7.



Figure 2-5 Charging conditions of sample [14]



Figure 2-6 Effect of mixing coke in case A [14]



They explained the difference as due to the reaction between the liquid slag with the high FeO content with coke above the ore layer when slag is rising up through the upper Al_2O_3 balls layer to the coke layer. The lowering of the gas permeability resistance is because the mixed coke added a new void to the ore layer.

Chen et al. [6] studied the effect of burden distribution on permeability in a packed bed. They found that as the layer thickness ratio L_{ore}/L_{coke} increased, the pressure drop increased under the range $L_{ore}/L_{coke} = 2$. The pressure drop could be decreased with increase of layer number and layer inclination angle in a packed bed with the same charging volume. They pointed out that the layer number had no influence on the total pressure drop under the same heights of the packed bed for the charging case of horizontal layers.

Wang et al. [7] studied the mixed charging of coke (10~60 mm) and ore (5~60 mm) in a 300 m^3 inner volume industrial blast furnace. They found that the permeability of mixed charging is better than layer charging when the coke content is less than 15 %. The structure of the cohesive layer is changed by mixed charging of coke and ore. Coke becomes the skeleton of the cohesive layer. They pointed out that the increase of the bulk density of the burden layer also has a positive influence to the blast furnace operation.

Gong and Du [15] analysed mixed charging in the blast furnace through theory and practice. They pointed out that the interface of ore and coke intensify the permeability resistance. However, the mixed charging can remove the influence of the ore and coke layer interface. They had a successful operation in Jinan steel company and Anshan steel company. They proved that mixed charging can improve blast furnace permeability and efficiency and can decrease coke rate.

Yaroshevskii et al. [2] studied the effect of nut coke smaller than 40 mm through calculation and industrial trials. The Ergun equation was adopted to evaluate the permeability of the coke and ore layer. They pointed out that nut coke of 5~15 mm has a significantly positive effect on the permeability. The fractions of 10~20 mm and 30~40 mm affect the permeability nearly the same degree. The effect is especially large when the first 30 % nut coke is charged. A further increase of nut coke has little influence on the permeability.

Watakabe et al. [8] studied a high coke mixed ratio charging technique in the blast furnace using an under load reduction test system. They found that the maximum pressure drop is decreased with increasing coke mixing ratio at high temperature. As the coke rate increased up to 10 wt%, the pressure drop decreased slightly. The applied size of sinter is 10~15 mm and coke size is 10~15 mm (small size) and 30~40 mm (lump coke).



Figure 2-8 Effect of coke mixing ratio on pressure drop [8]

Babich et al. [9] studied the effect of nut coke on blast furnace shaft permeability using cold flow models. Both of the DNTU (Donetsk National Technical University) rig and RWTH (RWTH Aachen University) rig were used to investigate the permeability when using nut coke. In DNTU tests (Figure 2-9), they found that mixing 10-20 % nut coke into an ore layer decreased the pressure drop very quickly compared with other portions. (Sinter: 3-5 mm, Nut coke: 3-5 mm).



Figure 2-9 Effect of nut coke on pressure drop [9]

In an RWTH test (Figure 2-10 and Figure 2-11), they found that the pressure drop decreased with increased nut coke rate (Sinter 8-12 mm, Nut coke 15-20 mm). This is very clearly at higher flow rate and Reynolds number. The permeability of the multi-layer is higher than of a single layer. This opinion is different from that of

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Chen et al. [6]. Babich et al. proposed that the number of boundary layers will cause the increase of the pressure drop.

Figure 2-10 Dependence of specific pressure drop on Re and flow rate for coke/burden layer thickness ratio 1:1 [9]



Figure 2-11 Dependence of specific pressure drop on Re and flow rate for coke/burden layer thickness ratio 1:2 [9]

Watakabe et al. [16] pointed out that the mixing coke can decrease the maximum pressure drop as shown in Figure 2-12. The maximum pressure drop stays at the same value or shows a small increase at 15 wt% mixing coke. Coke size is between 10-15 mm and 30-40 mm. An under load reduction experiment was conducted in their study.



Figure 2-12 Effect of mixed coke ratio and sinter ratio on permeability [16]

Short summary

Based on the above descriptions, it is found that most researchers concluded that adding nut coke into an ore layer is positive for improving permeability. However, several researchers found that permeability is not improved by nut coke addition. even the pressure drop goes up. The tested nut coke size and nut coke mixing ratio are different in each researcher's case. Most researchers mainly focused on 10~20 mm nut coke. As a conclusion a wider range of nut coke size should be further tested and the reasons for nut coke improving the permeability should be deeply studied.

2.1.2 Reduction kinetics

Ferrous materials in the blast furnace mainly consist of Fe_2O_3 and Fe_3O_4 . Removing oxygen from the ore burden is called reduction. The blast furnace process is based on the reduction behaviour of the burden ferrous materials. Reduction rate and reduction degree influence the production of the blast furnace directly.

The thermal reserve zone temperature in the blast furnace is approximately consistent with the starting temperature of the Boudouard reaction of coke (Equation 2-1), which involves intensive endothermic reactions. The Boudouard reaction controls the overall reaction inside the blast furnace. If the starting temperature of the thermal reserve zone can be lowered, the equilibrium

concentration of the FeO-Fe reduction reaction (Equation 2-2) will be shifted to higher CO gas utilization efficiency. This results in improved CO gas utilization efficiency at the furnace top and a decrease in consumption of reducing agents. Figure 2-13 shows [17] the relationships between furnace temperature and gas composition as plotted in the equilibrium diagram of the Fe-C-O system, which was obtained by a test to use a large amount of nut coke in a blast furnace of Kobe Steel in Japan.



Figure 2-13 The measured relationships between temperature and CO potential [17]

Isobe et al. [14] found that with a small amount (under 3 wt%) of coke mixed with ore in case A shown in Figure 2-5, the metal surrounding the mixed coke interface reacts with coke by direct reduction and the beginning temperature of the direct reduction becomes lower. In case B, however, the beginning temperature of direct reduction is not related with the mixed coke ratio increase and is almost constant at about 1070°C. This is because the liquid slag FeO could react with the coke layer above in case B. They concluded that when the mixed coke ratio is less than 3 wt% and the size is 8-11 mm, all mixed coke is consumed before melt-down. And the endothermic reaction occurs less rapidly than with mixed coke ratios over 3 wt%. In addition, the gas permeability can be improved in the cohesive zone.

Du et al. [4] observed by X-ray technology that mixed coke reacts with the softening ore materials. Reduction of the ore by mixed coke is obvious when using mixed charging. Molten slag and iron flow through one void to another void in the

mixed burden. Therefore, mixed charging changes the gas flow characteristics and enhances the reduction behaviour in the cohesive zone.

Gong et al. [15] published results from practice in an industrial blast furnace of Ansteel in China. The experiments have shown that the direct reduction degree changes from 0.52 to 0.568 when 80 wt% coke is added into the ore layer. Coke rate decreased with about 25 kg/THM and the blast furnace output increased with about 8 t/day.

Figure 2-14 shows that the reduction degree of mixed charging is higher than that of layer charging at high temperature. Yang and Yang [1] pointed out that the reduction degree of mixed charging below 1000 °C is close to layer charging. The reduction degree between 1000-1300 °C for mixed charging is higher than for layer charging.



Figure 2-14 Kinetic curves of reduction for layer and mixed charging at 900 °C and 1250 °C [1]

Figure 2-15 is a schematic view of the reduction process for layer and mixed charging [1]. The ore particle surface is softened and the pores within the particle are blocked during the iron ore reduction process. It makes the diffusion resistance much higher. Mixed charging will increase the diffusion, the partial pressure of CO in the sample bed and the contact area between ore and coke. Therefore the chemical reaction at the interface will be promoted. They concluded that the mixed charging reduction process is controlled by internal diffusion at 900 °C (before softening) and by internal diffusion and chemical reaction at the interface at 1250 °C (after softening).


Figure 2-15 Schematic view of reduction process for layer and mixing charging [1]

The thermal reserve zone temperature is approximately equal to the starting temperature of the carbon solution loss reaction (endothermic reaction) of coke [18-19]. Kasai et al. [17] found that mixing carbonaceous materials (including nut coke) into the burden layer lowered the thermal reserve zone temperature as shown in Figure 2-16. Differential thermal analysis was used in their research. The thermal reserve zone temperature decreased with an increase of the carbonaceous materials (including nut coke) ratio due to larger contact area between small size coke and iron ore.



Figure 2-16 Effect of the carbon content on the starting temperature of endothermic reaction [17]

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Further research was conducted by Natio et al. [20]. They found that the thermal reserve zone temperature decreased to 900 °C when mixing high reactivity coke with iron ore. They concluded that the thermal reserve zone temperature can be controlled by the reactivity of the coke. The thermal reserve zone temperature and the efficiency of the blast furnace will be improved when using high reactivity coke.

Mousa et al. [22-23] investigated the influence of nut coke on sinter reducibility. Mixing nut coke into a sinter layer improves the reduction behaviour by enhancing the CO potential through the Boudouard reaction. Nut coke in the sinter bed can not only improve the reduction behaviour of sinter but also results in smoother blast furnace operation. Mixing nut coke in the sinter bed has improved the sinter reducibility through improving the gas permeability.

Kim et al. [24] did a study on usage of nut coke in an industrial blast furnace. The optional ratio of nut coke in the sinter layer is 12.5 %, when it is ideally mixed and the diameter of sinter and nut coke is the same. The density difference between nut coke and sinter causes segregation of nut coke and sinter. Therefore, the burden distribution must be investigated and the charging mode must be adapted when using nut coke.

Short summary

The above discussions demonstrate that nut coke could be a kind of high activity coke due to its relatively higher specific surface area. The thermal reserve zone temperature could be decreased by high activity coke. A lower thermal reserve zone temperature will lead to a lower starting temperature of the Boudouard reaction. The CO potential increases with a lower starting temperature of the Boudouard reaction. Thus, all of the researchers concluded that adding nut coke in an ore layer has the ability to improve the reduction behaviour of the blast furnace. The mechanism of nut coke consumption is however not very clear.

2.1.3 Softening and melting behaviour

The area where ore starts to soften and melt is known as the cohesive zone. Softening and melting are physical phenomena and chemical changes in the cohesive zone behaviour are related to the location and shape of the cohesive zone and the gas flow, and have an important influence on the blast furnace operation.

Gono et al. [25] investigated the effects of mixing low quality ore with coke, finding that the reducibility and high temperature properties of the raw material are improved. Application of mixed charging at NSC Nagoya No. 3 blast furnace in Japan resulted in improvement of CO utilization by 0.4 % and reduction of the fuel ratio by 3 kg/tHM.

Isobe et al. [14], found that liquid slag is generated at about 1100 °C when the blast furnace is operated with separate coke and ore layers. Pressure drop increases very quickly at this temperature. When mixing coke into the ore layer, the slag melting temperature becomes higher. But when the mixing coke ratio is over 3 wt%, there is no obvious effect on this temperature. They explained this phenomenon by a contrasting case B. When the coke rate is less than 3 wt%, the liquid slag with high FeO will react with coke mixed in the ore layer and coke layer above. When the coke rate is over 3 wt%, the liquid slag reacts only with mixed coke in the ore layer.

Gong et al. [15] found that the cohesive zone character can be improved by mixed charging as it improves the mass and heat exchange in the cohesive zone. The thickness of the cohesive zone decreases and the high temperature zone shifts downward.

Du et al. [26] published that the softening and dripping temperature could be increased by mixed charging. The softening and dripping zone is narrowed when the mixed coke ratio is increased. They concluded that mixed charging improves the reduction of FeO and increases carburization of molten metal. Reduction of FeO causes softening and dripping temperature to increase. Increased carburization has a positive effect on the molten iron dripping as it lowers the melting temperature of the Fe-C alloy.

According to Yang and Yang [1], mixed charging has little effect on softening and melting behaviour. The effect of coke size and mixing coke ratio on softening and melting are not obvious.

Based on laboratory equipment under simulated blast furnace conditions, Hsieh and Liu [27] concluded that softening and melting temperature can be increased from 1222 °C to1470 °C and from 1522 °C to1553 °C, respectively, by mixing nut coke into ferrous burden. The nut coke size is 8-10 mm and coke ratio in the mixed layer is 3 wt%. Further research showed that nut coke size of 6.3-8 mm added into the burden layer deteriorated the softening properties. Therefore, too small nut coke will have a negative effect on the softening and melting behaviour

Watakabe et al. [8] pointed out that the temperature of metal melting-down reaches a maximum when the mixed nut coke ratio was 10 wt% in their high temperature tests, as can be seen in Figure 2-17.



Figure 2-17 Temperature of metal melting-down [8]

Short summary

Some researchers found that adding nut coke into an ore layer could increases the softening and melting temperature under their specific experimental conditions. However, several researchers concluded that nut coke cannot increase the softening temperature. The effect of nut coke on softening and melting properties should be clarified.

2.1.4 Industrial practice

Because each blast furnace is unique and operates under unique conditions it is difficult to draw general applicable conclusions from this comparison. It just gives an overview of the industrial practise of adding nut coke to the ferrous burden layer. It is based on the MSc thesis of M. Bos [28].

Not every company applies the same definition of nut coke. The undersize is a key to implement a successful nut coke strategy. If particles are too small or the size distribution is too wide the performance of the furnace will decrease [29]. Some companies in different countries conducted some practices on adding nut coke into ferrous burden.

In Europe, the usage of nut coke up to 100 kg/tHM and more is practiced in blast furnaces. Nut coke may enhance the gas distribution in the wall area [30]. This reduces the possibility that ore particles are not melted completely before reaching the tuyere level. In Asia, South Korean and Japanese companies tried to mix nut coke into ferrous burden. POSCO (Korea) used nut coke in their blast furnaces from many years ago [31]. The furnace permeability in the mid area is improved. Unfortunately, there is no public data about the amount of nut coke used in their blast furnaces. Mixing methods were also tested for adding nut coke into the ore layer in NSC's blast furnaces at Kimitsu works in Japan [32]. The most stable

operation was achieved when the coke was mixed uniformly with the first ore batch. There is also no further open comments from Kimitsu works. In Russia, the usage of nut coke varies between 6 kg/THM and a maximum of 24 kg/tHM at different plants.

2.2 Experimental techniques for studying blast furnace

2.2.1 Cold flow model

A cold flow model is a very useful approach for studying metallurgical process, mainly for streaming conditions. It has many advantages compared with high temperature experiments, for instance low cost, easy manufacturing, convenient operation and measurement and short test period. It is widely used to study the gas or liquid flow in the packed bed of a blast furnace. Pressure sensors are used to measure the pressure drop of a packed bed. Some models use X-Ray or optical camera to record the internal phenomena in the packed bed. Some models camera the effect of particle shrinkage on the permeability layer.

Szekely and Propster [33] used a physical model to measure the flow resistance of layer charged burdens, using industrial materials. This model can measure the pressure profile (both axial and radial) as a function of the gas flow rate in a packed bed layer, charged with typical blast furnace burden materials. Figure 2-18 shows a schematic sketch of the apparatus. The material was contained in a cylindrical column, 0.97 m in diameter and 1.07 m in height, which was placed on a wind box, the dimensions of which are indicated in the figure. The choice of the relatively large column diameter was dictated by the need to minimize wall effects.



Figure 2-18 Schematic view of the experiment facility [33]

Chen et al. [6] established a model to study the gas flow in a packed bed. Figure 2-19 illustrates a schematic diagram of the experimental apparatus. The apparatus was so constructed as to allow the convenient measurement of the gas velocities and the pressure profiles in both axial and radial directions under the various conditions of the gas flow rate and the layer structure in the packed bed. A transparent acrylic pipe with 149 mm in diameter and 700 mm high is used as a cylindrical column.



Figure 2-19 Cold flow model apparatus [6]

The packed bed is changed in the layer-by-layer structure with different inclination angles of 7.7', 15.0' and 21.9', and the height of the packed bed was 420 mm. Nitrogen cylinders are used to provide the gas. The gas flow rate is measured by a rotameter and controlled over a range of 100 to 500 NL/min, and the gas is introduced into the bottom of the apparatus and flow into the packed bed through thousands of holes of 2 mm in diameter at the wall side in order to keep the inlet gas flow circumferentially uniform. Alumina balls and a binary mixture of glass beads are used as the packing materials to simulate the coke and ore layer in a blast furnace, respectively, which has different void fractions.

Raichura [34] did a study about pressure drop and heat transfer in a packed bed. A physical model was used in his study to measure velocity distribution and pressure drop in a cylindrical packed bed (Figure 2-20). Compressed air, delivered to the circuit via a pressure-regulating valve, is channelled into either one of two pipes in parallel. The flow is controlled by gate valves and its rate is measured by standard orifice meters installed in each section. The air then flows through a common section before entering the vertical test section assembly. The particles used in

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these experiments are stainless spheres of diameter I, 3, or 5 mm and near spherical glass beads of diameter 3, 5, 8, or 10 mm in different experiments.



Figure 2-20 Schematic view of the experiment equipment [34]

Babich et al. [9] adopted a physical model to investigate the effect of nut coke on blast furnace shaft permeability. The model was designed as a set of plexiglass segments. The geometry of the model is shown in Figure 2-21. Air is blown via six tuyeres and streams through the packaged bed. The air flow is measured and controlled by a flow meter. Pressure drop in the packaged bed is measured by a U-tube manometer. The effect of layer thickness, gas velocity and flow rate on the pressure drop in different packed beds is examined. Packed bed height is kept 500 mm in all tests. The ratio of the packed bed height to the stack diameter corresponds roughly to the H/D ratio of the furnace "dry' zone.



Figure 2-21 Schematic view of cold flow model [9]

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Ishii [35] developed a model of the gas permeability of cohesive layers. Test work was conducted at room temperature. Sponge balls filled with high viscosity liquid are settled in an acrylic reactor. The packed bed is pushed from the upper side. Air is ventilated from the lower side. High viscosity liquid is pushed out from the sponge balls as they shrink. Liquid flow is observed using a video camera, and the pressure drop of air through the bed is recorded.



Figure 2-22 Schematic view of cohesive zone model [35]

Short summary

A cold flow model is a useful tool to study the gas flow in the blast furnace. Most of the models only simulate the blast furnace "dry zone". There is also a model that can simulate the cohesive zone. Almost all models are equipped with a pressure sensor or more sensors to measure the pressure drop. All these models are rarely used to study the effect of nut coke on permeability except the model used by Babich [9].

2.2.2 High temperature experiments

Almost all processes of ferrous metallurgy are conducted under high temperature conditions. Therefore, high temperature testing is widely used in the metallurgy field. It can simulate the high temperature region in a metallurgical reactor and provide theoretical data for industrial plant. There are several kinds of high temperature furnaces existing in present, such as electric resistance furnace, induction furnace, and electric arc furnace. The most common used laboratory scale reactor in the ferrous metallurgy field is the electric resistance vertical tube furnace.

Chapter 2 Literature review

Hessien et al. [36] designed a vertical tube furnace equipped with six SiC heating elements and controlled by a SCR power regulator used for heating samples (Figure 2-23). The geometrical change of samples during the reduction experiments is measured using an X-ray transmission system and recorded by a video recorder. The reducing gas is prepared by mixing the gas components, whose flow rates are controlled by the respective mass flow controllers (MFC). The CO and CO₂ contents in the outlet gas are analysed using a QMS gas analyser. The total flow rate of outlet gas is measured by a wet gas flow meter. Temperatures, output of MFC, wet gas flow meter and QMS are recorded by the data acquisition system equipped with a computer for data analysis.

The diameter and height of the graphite crucible is 23 mm and 100 mm, respectively (Figure 2-24). A coke plate (20 mm×10 mm) is trimmed off and placed on the sinter. The uniform flow of reducing gas is made possible through 72 holes of 0.8 mm diameter at the bottom of the graphite crucible.



Figure 2-23 Schematic diagram of heating reduction experimental apparatus [36]



Figure 2-24 Graphite crucible assembly [36]

Geassy et al. [37] did some study on the reduction behaviour of iron ore fluxed pellets under load and his apparatus details are as following (Figure 2-25). The furnace is heated up in a flow of purified nitrogen till it reaches the required temperature and kept constant for 15 minutes. Then N₂ is replaced by 4.0 L/min of the reducing gas mixture. The weight-loss resulted from the removal of oxygen during reduction process (Fe₂O₃ to Fe) as a function of time is continuously recorded by the aid of a thermo-balance (K). The output of the balance is attached with a recording unit under controlled operational conditions. (K: Electronic balance, S: Stainless steel chain, W: Standard weights, P: Piston, a: upper disk (5.8 cm diameter), b: lower disk (3.8 cm diameter), N: Reaction tube (L-90 cm, D-5.8 cm), M: Temperature control unit, F: Electrically heated furnace, L: Thermocouple).



Figure 2-25 Schematic view of the test furnace system [37]

Watakabe et al. [8] studied a high coke mixed ratio charging technique to the blast furnace by an under load reduction test system. This system has a carbon heater which is separated from the reduction gas by a high-alumina tube (Figure 2-26). The crucible (Φ 100 mm) is made of carbon and has carbon distributors at its top and bottom. The specimen is loaded by an automatic weighing system. Dripped metal and slag are collected at a water cooled sampling plate below the furnace tube. In this experiment, CO–CO₂–N₂ mixed gas is introduced into the furnace tube while controlling the gas composition with an automatic controller. The flow rate is 5×10^{-4} Nm³/s. Outlet gas collected from the furnace top is analysed every 120 s by gas chromatography. The heating pattern, gas composition and the load are automatically controlled.

Kaushik and Fruehan [38, 39] did experiments to study the mechanism of softening and melting and impact on the cohesive zone through ISM (Industrial Softening and Melting). Figure 2-27 is a schematic view of the ISM. In their experiment, the lump ore and direct reduced iron (DRI) pellets are sieved into a size range 12– 14 mm. The SM test is conducted in an electric tube furnace. Approximately 500 g lump ore sample is sandwiched between two coke layers in a graphite crucible (8 cm inner diameter and 22 cm long). The briquettes were cut into half and stacked vertically side by side. The voids between them are filled with the coke pieces. The height of the ferrous burden in the graphite crucible is 8 cm. The sample temperature is recorded using a thermocouple which is positioned above the top coke layer. The dripped material is collected in a melt collection pot located at the bottom of the furnace. The furnace and sample temperature, bed shrinkage and gas pressure drop across the burden bed are continuously measured.



Figure 2-26 Schematic view of under-load-reduction test system [8]



Figure 2-27 Industrial softening and melting (ISM) test [38-39]

Nogueira, et al. [40, 41, 42, 43] designed an experiment to investigate softening and melting phenomena in the blast furnace under the conditions of mixed burden. Figure 2-28 is a schematic of the experimental apparatus used for SM (Softening and Melting) experiments. 1: transducer for displacement measurement; 2: sample arranged in three layers; 3: gas outlet to mass spectrometer (MS); 4: output thermocouple in alumina plunger; 5: graphite crucible with burden (six samples); 6: graphite support; 7: thermocouple to furnace control; 8: graphite pusher; 9: gas inlet; 10: pressure gauge. The CO and CO₂ content of the outlet gas is analysed using MS. Only the outlet gas is analysed in each SM experiment. Since the gas inlet is not in the hot zone, the profiles of the inlet gas are taken twice independently by running the MS for a long time (12 h). They are found to be identical having similar compositions of CO and CO₂. These gas compositions are therefore assumed to exist in the inlet gas streams for the entire duration of all experiments. The burden is weighed and then stacked in a graphite crucible (26 mm inner diameter and 64 mm long) and the initial bed height is measured.



Figure 2-28 schematic of experimental apparatus used for SM experiment [40]

Kasai and Matsui [17] designed a DTA experiment to study the thermal reserve zone temperature in the blast furnace. In Figure 2-29 the experiment apparatus applied in their research is presented. The reaction tube has an inner diameter of 140 mm and the sample basket has a diameter of 120 mm and a height of 150 mm. The standard material is a 10 mm alumina ball. The top end of the thermocouple is set at the centre of the height and the width of the sample bed and standard material bed. The rate of temperature increase for the standard material is set constant at 5 °C/min. The gas composition is set to the constant pattern, which simulates those of an industrial blast furnace.



Figure 2-29 Experimental apparatus [17]

The standard material is heated from room temperature to 1250 °C under the above conditions. The temperatures of the standard material and the sample are measured simultaneously and the difference in both temperatures is obtained. The starting temperature of the endothermic reaction of the sample is obtained from the extrapolated starting temperature.

Naito et al. [20] established an experiment to study the thermal reserve zone temperature. Figure 2-30 below is the experiment apparatus applied in their research. They developed a counter-flow, moving-layer type adiabatic blast furnace inner reaction simulator (BIS) to confirm the effect of the technology. The reaction tube is a stainless steel pipe 103 mm in inner diameter and 5.4 m in height. The electric furnaces consist of four heating furnaces that preheat the gas to the temperature of the upper cohesive zone of a blast furnace (1200 °C) and complete the reduction of ore and 10 heat-insulating furnaces that make the reactions and heat transfer at temperatures lower than the above temperature proceed in an adiabatic system.

Tata steel established an apparatus for reduction experiment of iron ore [44]. Figure 2-31 is schematic view of the equipment system. N₂, CO, CO₂ and H₂ are mixed in the gas mixing chamber and then flow into the furnace. There is a slag collector under the furnace for collecting the molten iron and slag. The outlet gas is measured by a CO-CO₂ analyser. The sample temperature is recorded with time during the experiment process.



Figure 2-30 Schematic representation of the adiabatic blast furnace simulator (adiabatic BIS) [20]



Figure 2-31 Schematic view of the apparatus in Tata steel [44]

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The Advanced Softening and Melting (ASAM) apparatus was designed by British Steel in order to simulate the behaviour of the burden in the cohesive zone [28]. During the ASAM test, it runs on a simulated blast furnace gas and temperature profile. Figure 2-32 is a schematic view of the ASAM facility. General dimensions of the graphite sample holder are 65.3 mm inner diameter and a height of 200 mm. In the sample holder the particles (sinter, pellet and coke) are present in sizes ranging from 10 to 15 mm.



Figure 2-32 ASAM measurement devices [28]

The HOSIM (Hoogoven Simulatie Model) is used at Tata Steel IJmuiden (before Hoogovens and Corus) as a production quality control tool for the ferrous burden materials in the upper part of the furnace [45]. In the HOSIM test, the weight changing of sample could be recorded by a balance. The experiment starts with preheating the sample under nitrogen gas to a temperature of 450 °C. The reduction starts when the gas composition is changed to blast furnace conditions.

BRASS is short for Blast furnace Reduction And Softening Simulation. The simulation of the blast furnace process is based on the results of vertical probing conducted at blast furnace 6 at Tata steel Ijmuiden [45].

J. Sterneland [46] used a high temperature experimental system shown in Figure 2-33. The size of the sample crucible (graphite) was 80 mm in diameter and 125 mm in height. The sample bed was 500 g. Above and below the sample bed

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30 mm layers of coke were placed. The furnace was placed around the ceramic tube and a loading ram above the sample crucible applied onto the sample bed.



Figure 2-33 A schematic view of the reduction under load equipment [46]

Short summary

High temperature equipment used in softening/melting/reduction experiments aims to simulate the physical and chemical changes in the cohesive zone of the blast furnace. Although various laboratory setups for this purpose have been developed, with similar apparatuses and procedures, none have yet been standardised. One reason is that in these kinds of simulations it is sometimes difficult to choose the experimental conditions because of lack of knowledge of the conditions in the high temperature zones of the blast furnace. Furthermore, when the experimental conditions have been chosen according to the operation of one blast furnace, those conditions would probably not apply to another furnace. Most of the facilities cannot measure pressure drop, the contraction of sample bed, weight changing and off-gas composition at the same time in one facility. They are only equipped with a part of these sensors. An advanced equipment should be constructed to obtain more comprehensive information from reduction, softening and melting experiment.

2.3 Summary

Literature study shows that mixing coke into the burden layer is a highly interesting item for research and development. Although several studies on mixed charging have been published, it still has the potential to be further deeply explored regarding its underlying mechanism. From the literature review, we get the following conclusions

- Permeability could be improved by mixing coke into an ore layer (mixed charging). An optimum range is found when the coke mixing ratio is between 10~15 wt%. Some researchers pointed that out the pressure drop is also decreased with the increase of layer number and angle. H₂ addition also has effect on the pressure drop of a sinter bed.
- The mixed charging technique has the ability to enhance the reduction characteristics of the iron ore. It lowers the temperature of the Boudouard reaction which improves the CO gas utilization efficiency at the furnace top and decreases the reducing agents rate. The reduction degree of ore with mixed charging is higher than that with layer charging at high temperature. Mixed charging decreases the coke rate and increases the output of the blast furnace.
- The softening and melting behaviour of mixed charging is better than the normal layer charging in blast furnace. The softening temperature could be increased and the cohesive zone thickness could be decreased when coke is mixed in the ore layer. It improves the high temperature properties of the cohesive layer.
- A review of the equipment used for research of iron ore reduction and gas flow in packed beds has been presented. It shows that under load high temperature testing and cold flow models are widely adopted in previous studies. Equipment used in reduction experiments is aimed to simulate the physical and chemical changes in the cohesive zone and/or thermal reserve zone of the blast furnace.

In literature there are many papers published about adding nut coke into an ore layer. Most of the researchers concluded that nut coke has the ability to improve the performance of the blast furnace. But, there is still space left for further study the effect of nut coke on the performance of the blast furnace. The mechanism is still not very clear and a wider range of nut coke size and a higher nut coke mixing ratio should be tested to evaluate the usage of nut coke in the blast furnace.

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3. COLD FLOW MODEL EXPERIMENTS

3.1 Introduction

Cold flow modelling is a very important research approach in study of metallurgical processes. It has various complimentary advantages compared to high temperature testing, for example, low cost, short test period, easy operation and measurement. It can be conducted at low temperature. The diameter of a high temperature furnace on laboratory scale is limited to 100-200 mm by technology, Therefore, it is very difficult to test big sized coke. However, a cold flow model can be made to test real size coke and iron ore in the blast furnace.

A cold flow model study was established to investigate the effect of mixing nut coke into the burden layer on the permeability in the blast furnace "dry zone". The effect of nut coke size, mixing nut coke ratio, layer numbers and gas flow rate on the pressure drop of a packed bed was investigated. These results will provide further knowledge for industrial practice with respect to the "dry zone". It will also provide the reference for the design of high temperature experiments of softening and melting and reduction when using nut coke in the ferrous burden performed in this study.

3.2 Experimental conditions

Based on the similarity theory, it is very difficult to satisfy all the similarity conditions between prototype and model at the same time. Gas flow in a packed bed is mainly related with Reynolds number (Re). It is widely accepted that the measurement results of the model are representative for the prototype when Re number similarity is achieved between the prototype and the model.

The Reynolds number varies from 500~5000 (based on the particle diameter in the packed bed) in an industrial blast furnace [1]. To keep the similar gas flow status between the prototype and the model, we must keep the same Reynolds number range for the industrial blast furnace and the cold flow model. Reynolds numbers from 500 to 1000 was applied in this experiment under laboratory conditions. Compressed air is applied instead of hot blast furnace gas. The maximum gas flow rate is 1 dm³/min in MSE Lab of TU Delft. That's the reason for adopting Reynolds numbers not close to 5000.

Table 3-1 Reynolds number and gas flow rate

	Re=500	Re=1000
U_m	0.12 m/s	0.24 m/s
Q	0.5 dm³/min	0.95 dm ³ /min

Table 3-2 Parameters of blast furnace and model

	Blast furnace	Model
Pressure (atm)	2	1
Temperature (°C)	1000 °C	20 °C
Gas composition	Blast furnace gas	Air
Density (kg/m ³)	0.56	1.205
Viscosity (Pa.S)	4.8×10 ⁻⁶	17.7
Inner diameter (m)	-	0.29
Cross-sectional area (m ²)	-	0.066019

The Reynolds number is calculated by:

$$Re' = \frac{\rho_m d_m U_m}{\mu_m (1 - \varepsilon_m)} = \frac{\rho_p d_p U_p}{\mu_p (1 - \varepsilon_p)}$$
(3-1)

where ρ_m and ρ_p are gas densities, d_m and d_p are average particle diameters, U_m and U_p are gas velocities, μ_m and μ_p are dynamic viscosities, and ε_m and ε_p are the voidages of the model and the prototype, respectively.

3.3 Methods and materials

3.3.1 Experimental facilities

The cold flow model is made of Plexiglas segments. The facilities are shown in Figure 3-1 and Figure 3-2. The inner diameter and height of the model are 290 mm and 800 mm, respectively. There are four tuyeres distributed on the lower part of the model. A differential pressure sensor is used to measure the differential pressure between top and bottom of the packed bed. Industrial samples of sinter/pellet and coke are randomly charged into the reactor from the top and the compressed air is blown into the model from the tuyeres. The gas flow rate is controlled by flow meters.

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Figure 3-1 Schematic view of the cold flow model facility

Figure 3-2 Picture of the cold flow model facility

Table 3-3 Measuring devices used in cold flow model experiment

Devices	Number	Range
Flow meter	4	0~0.3 dm ³ /min
Differential pressure sensor	1	0~200 Pa/0~500 Pa

3.3.2 Test Materials: pellet, sinter and coke

Industrial pellet, sinter and coke are used in this study. The information of materials is listed in Table 3-4.

Table 3-4 The size and packing density of materials

Materials	Pellet	Sinter	Nut coke
			10~15
	10~13	10 15	15~20
Size range (mm)		10~15	20~25
			25~30
Packing density (kg/m ³)	1663	1479	413~455



Figure 3-3 Illustration of tested materials: pellet (A), sinter (B) and coke (C)

3.3.3 Charging pattern

The coke layer is filled with 40~50 mm standard coke (packing density: 413 kg/m³), which is the normal size in an industrial blast furnace coke layer. The ore layer is a mixture of iron ore and nut coke. The coke mixing ratio is the weight percentage of the total coke in the blast furnace. For example, a coke mixing ratio of 20 % means that 60 kg nut coke is mixed with ore and 240 kg coke is in the coke layer under a constant coke rate of 300 kg/tHM [2].

The thickness of the pure pellet and sinter layer is fixed at 400 mm. It is almost half the thickness of the ore layer in an industrial blast furnace (a typical thickness of an ore layer is 700 mm) [2]. The weight of pellet and sinter are 44 kg and 39 kg, respectively, used in this study. To produce 1 ton hot metal needs 1580 kg ore [2]. This gives a ore/coke mass ratio of 1580/300 (i.e. 5.267). The weight of coke layer is calculated based on a coke rate of 300 kg/tHM as shown in Table 3-5 in the absence of nut coke. The thickness of the coke layer decreases as the nut coke mixing ratio becomes higher in the ore layer. The total weight of iron ore and coke is kept constant.

Γable 3-5 Weight and thickness of	ore layer and	coke layer
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	Pellet	Sinter
Weight of ferrous burden* (kg)	44	39
Thickness of ferrous burden* (mm)	400	400
Coke layer weight (kg)	8.34	7.42
Coke layer thickness (mm)	310	270

*In the absence of nut coke in the ferrous burden.

Four charging patterns were adopted in the experiments and Figure 3-4 shows the schematic view. Figure 3-4A shows one ore layer charging (no normal coke layer). Different nut coke mixing ratios were tested to study the effect of adding nut coke on the pressure drop in the ore layer. Figure 3-4B shows two layers charging. Two layers charging means one coke layer on the bottom and one ore layer on the top. Adding nut coke into the ore layer means that the thickness of the coke layer decreases under a constant coke rate. It is known that the thickness of the coke layer is an important issue for blast furnace permeability. A balance has to be made between adding nut coke and keeping a proper thickness of the coke layer. Thus, the purpose of two layer charging is to find the optimum mixing nut coke ratio. Figure 3-4C and Figure 3-4D show the four layers charging and six layers charging is to obtain the effect of layers number on the pressure drop under the same burden weight and coke weight. The same weight of the total iron ore and coke is kept for all charging patterns.



A: one layer charging, ore-nut coke layer, B: two layers charging, one ore layer and one coke layer C: four layers charging, two ore layers and two coke layers D: six layers charging, three ore layers and three coke layers

Figure 3-4 Schematic view of charging patterns

In Table 3-6, the feeding materials, nut coke mixing ratio, and layers number adopted in this study are listed. Three series of experiments (pellet, sinter and their mixture) were tested. Mixing all coke into the ore burden is still an argument in industry. The coke layer still plays the key role in the blast furnace, to provide mechanical support to the charge column, to influence gas distribution throughout the blast furnace and to act as a permeable bed. Therefore the mixing ratio in industry is not beyond 50 % [2].

Feed materials	Mixing coke ratio. %	No. of lavers			
Pellet with coke	0, 10, 20, 30, 40	1, 2, 4, 6			
Sinter with coke	0, 10, 20, 30, 40	1, 2, 4, 6			
Mixture with coke*	0, 10, 20, 30, 40	1, 2, 4, 6			
(*65 % sinter and 35 % pellet [2])					

Table 3-6 Experimental plan

3.4 Pure coke and/or iron ore bed

From the physical aspect, the inner structure of the upper part of a blast furnace is a packed bed. The packing pattern, porosity, particle size and its distribution determine the permeability and gas dynamics of the packed bed. Thus, a series of layers of pure raw materials were tested to explore the original gas dynamics of the packed beds under different size of materials.

Figure 3-5 shows a function of the compressed air flow rate evolution of the pressure drop with different coke size. For all coke size, the pressure drop goes up with increasing gas flow rate. It can be clearly seen that the pressure drop for small sized coke is higher than for large sized coke. In the ideal theory of packing, the porosity is not related with particle size. It is just determined by the arrangement of the particles. However, the test shows different results. Porosity measurement and the calculated porosity based on the Ergun's equation reveal that the porosity of a large sized coke bed is larger than with small sized coke shown in Table 3-7. The reason for this phenomenon is that it is impossible to keep all industrial raw materials in the same size. Generally, the raw materials have a size distribution. It will generate a multi-granular packed bed. Although the size distribution is kept as narrow as possible, it still cannot obey the ideal theory of packing. Irregular shape and different size of particles will reduce the porosity of the packed bed. If the particles are packed in a certain packing pattern, the small sized particles will fill into the void between the large particles. Thus different sized coke may cause a different porosity and then influence the pressure drop and permeability.



Figure 3-5 Pressure drop of a different size coke bed

Table 3-7 Comparison of measured and calculated porosity of coke packed bed

Nut coke size range (mm)	10~15	15~20	20~25	25~30	30~40	40~50
Measured porosity	0.4956	0.5027	0.5289	0.5415	0.5497	0.5691
Calculated porosity	0.4762	0.4995	0.5369	0.5565	0.5572	0.5765

To investigate the properties of a packed bed of ferrous materials, a pure pellet packed bed and a pure sinter packed bed were tested, respectively. Figure 3-6 shows that the pressure drop of sinter is lower than of pellets under the same condition. It is mainly due to the difference in shape of pellet and sinter. A pellet is almost a sphere and sinter has no regular shape. Pellets contact with each other in a relatively compact way and strive to form a dense packing pattern. Sinter possesses irregular shapes and may generate "bridges" in a packed bed. Moreover, the sinter itself is a porous material. Table 3-8 shows the measured porosity and calculated porosity based on the Ergun equation of pure sinter bed and pure pellet bed. It demonstrates that the porosity of sinter is bigger than pellet from both porosity determination methods. Therefore the permeability of a packed bed of sinter is larger than of pellets. The comparison results of the two methods indicate that they agree quite well.





Table 3-8 Comparison of measured and calculated porosity of iron ore bed

Iron ore	Pellet	Sinter
Measurement porosity	0.4312	0.4997
Calculated porosity	0.4397	0.4886
The porosity is measured	by water w	ith a column

3.5 One layer testing

One layer charging (ore-nut coke mixed charging) means only an ore layer, no coke layer, just mixing a certain amount of nut coke in the ferrous burden (pellet and sinter). The experiment aims to know the influence of nut coke on the permeability of just an ore layer.

		Iron ore mixed with nut coke										
	0%		0%		10)%	20)%	30)%	40)%
	wt	ht	wt	ht	wt	ht	wt	ht	wt	ht		
	(kg)	(m)	(kg)	(m)	(kg)	(m)	(kg)	(m)	(kg)	(m)		
Pellet	44	0.4	44.8	0.42	45.7	0.44	46.5	0.46	47.3	0.48		
Sinter	39	0.4	39.7	0.43	40.4	0.46	41.2	0.49	42.0	0.52		
	*wt: weight, ht: height											

Table 3-9 Weight and height of the sample bed

The packing density of a packed bed determines the porosity and could be divided in three ways:

• Loose packing density: The particles are filled into a defined volume without any compressive force (shown in Figure 3-7A).

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- Tap density: The particles are compacted by shocks in horizontal direction (shown in Figure 3-7B).
- Vibrating density: The particles are compacted by vibration in vertical direction (shown in Figure 3-7C).



Figure 3-7A Loose packing



Figure 3-7B Tap packing



Figure 3-7C Vibrating packing

The upper zone of the blast furnace is assumed to have the loose packing. It is affected neither by shocks in the vertical direction nor by vibration in the horizontal direction. It just receives the force due to the mass gravity of the above burden.

3.5.1 Effect of nut coke mixing ratio

Figure 3-8 shows the compressed air flow rate as a function of the pressure drop with different nut coke mixing ratios. For all mixing ratio conditions, the pressure drop goes up with increasing gas flow rate. The pressure drop of all mixing ratios changing from 10 % to 40 % is smaller than for the pure ore layer (0 % mixing ratio). The total volume of packed bed increases when adding nut coke into ferrous burden.



Figure 3-8 The effect of 10~15 mm nut coke on the pressure drop of pellet layers under different air flow rates and at different mixing ratio

Figures 3-9 show the effect of mixing ratios on the pressure drop for different sized nut coke. It can be seen that for all four cases, the pressure drop goes down with the increase of nut coke mixing ratio. It indicates that adding nut coke will improve the permeability of the ore layer and more nut coke will bring on better permeability when the mixing ratio is less than 40%. The reason is that nut coke increases the porosity of the packed bed and it also increases the average diameter of particles in the packed bed. Table 3-10 and Figure 3-10 indicates that the porosity increases with the increase of nut coke mixing ratio for each sized nut coke, the porosity increases when adding 10 % and 20 % nut coke. The porosity decreases when adding 30 % and 40 % nut coke into the ferrous burden. This could be caused by small particles (pellet) filled in the gap of big particles (nut coke) when the mixing ratio is higher than 30 %. It reduces the porosity of the mixing bed.



Figure 3-9 Effect of nut coke size and mixing ratio on the pressure drop, gas flow rate: 1 dm^3 /min

Table 3-10 Calculated porosity of mixed charging bed (pellet mixed with nut coke)

	10~15 mm	15~20 mm	20~25 mm	25~30 mm
10 %	0.4369	0.4217	0.4081	0.4152
20 %	0.4465	0.4311	0.4172	0.4251
30 %	0.4627	0.4401	0.4195	0.4245
40 %	0.4691	0.4422	0.4316	0.4211



Figure 3-10 Effect of nut coke size and mixing ratio on the porosity

3.5.2 Effect of nut coke size

From Figure 3-9, it also can be seen that the effect of nut coke size on the pressure drop at the flow rate of 1 dm^3 . The size of 10~15 mm nut coke is better than other size ranges to obtain a lower pressure drop under this experimental condition. The porosity of nut coke 10~15 mm is higher than other cases shown in Table 3-10. It explains why 10~15 mm nut coke is better than other size nut coke for improving permeability. The differences among other sized nut coke (15~20 mm, 20~25 mm and 25~30 mm) are in one trend. It is hard to say which one is better. It could be explained by the balance between a decreased porosity and an increased particle diameter. Future work should be done for exploring a deeper understanding of the mechanism based on particle science and engineering.

Sinter mixed with different sized nut coke was also tested in this study, which shows similar performance with the case of pellet as shown in Figures 3-11. It is clearly shown that the mixing ratio of nut coke at 20% gives the lowest pressure drop or the highest permeability.



Figure 3-11 Effect of nut coke size and mixing ratio on the pressure drop (15~20mm nut coke mixed with sinter)

3.6 Two layers testing

An industrial blast furnace is charged with alternating layers of coke and iron ore containing burden. At a constant coke rate, adding nut coke into an ore layer means that the thickness of the coke layer decreases when the nut coke mixing ratio increases. Thus, 2 layer charging tests were conducted to investigate the effect of nut coke on the pressure drop of an alternating layers packed bed. Coke size is 40~50 mm as used in the coke layer. Different types of iron ore (pellet, sinter, mixture of pellet and sinter) mixed with differently sized nut coke were tested.

3.6.1 Pellet mixing with nut coke

Figure 3-12 shows that the pressure drop goes down when nut coke is mixed with pellets. It only has a tiny difference after 10 % mixing for 10~15 mm nut coke. Figure 3-13 indicates that for the pellets mixed with 15~20 mm size nut coke the pressure drop decreases evidently when the mixing ratio is less than 30 %. It can be seen that the pressure drop goes down when the mixing ratio changes from 0 to 20 %. It goes up when the mixing ratio changes from 20 % to 40 %. One can conclude that 20 % is the optimum mixing ratio. Figure 3-14 and Figure 3-15 show a similar trend as Figure 3-15 for larger sized coke particles. The only difference for Figure 3-14 is that the optimum mixing ratio is now 30 % for 20~25 mm nut coke. More nut coke could be used due to only a small increase in pressure drop for 40 % nut coke.

One layer testing shows that adding nut coke will improve the permeability and that the pressure drop goes down with increasing nut coke mixing ratio. However, two layers testing indicates that the pressure drop goes down firstly and then goes up at a certain nut coke mixing ratio, for instance, 20 % and 30 %. The differences between the two types of tests prove that the thickness of the coke layer has a significant effect on the permeability when adding nut coke in the iron ore layer. Thus a balance has to be made between adding nut coke and keeping a proper thickness of the coke layer. Through a series of tests, the best balance is obtained and the optimum mixing ratio is found to be 20 % and/or 30 % to achieve the best permeability under the laboratory conditions.





Figure 3-12 The effect of 10~15 mm nut coke on the pressure drop of a pellet layer, flow rate 1 dm³

Figure 3-13 The effect of 15~20 mm nut coke on the pressure drop of a pellet layer, flow rate 1 dm³









3.6.2 Comparison of different iron ores

Pellets and sinter are the standard iron containing materials used in a blast furnace. Cold flow model experiments were conducted under room temperature. They only focused on the physical characteristics and did not consider the chemical properties. Pellets are near spheres (shown in Figure 3-16) of typically diameter 9–16 mm [1]. A size of pellet of 10~13 mm is used in the cold flow model experiment.



Figure 3-16 Iron ore pellet



Figure 3-17 Nut coke

Sinter consists of non-spherical particles and the size distribution is around 10-25 mm. A picture of sinter is shown in Figure 3-18. Sinter is made in three different types: acid, fluxed and super-fluxed sinter. The properties of sinter are dependent on the blend type and chemical composition. The size distribution of sinter used in the cold flow tests is 10~15 mm.
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Figure 3-18 Iron ore sinter

Sinter

Figure 3-19 to Figure 3-22 shows that the pressure drop decreases when the coke mixing ratio varies from 0 % to 40 %. When the mixing ratio is higher than 20 %, the pressure drop goes up again. The optimum mixing ratio is 20 % for this condition. 15~20 mm and 25~30 mm nut coke mixed with sinter were also tested. They demonstrate a similar trend with the case of 10~15 mm and 20~25 mm nut coke.



Figure 3-19 The effect of 10~15 mm nut coke on pressure drop of sinter layer under different flow rates







Figure 3-20 The effect of 10~15 mm nut coke on pressure drop of sinter layer, flow rate 1 dm³





Mixture of pellet and sinter

In an industrial blast furnace, the ore burden consists of a mixture of sinter and pellets, even with mixing some lump ore into the burden layer. Thus the effect of nut coke on the pressure drop of a sinter-pellet mixture packed bed was investigated. The weight percentage of sinter is 65 % and pellet is 35 %. Mixing of nut coke was tested in four sized ranges (10~15 mm, 15~20 mm, 20~25 mm and 25~30 mm). Spherical pellets are mixed with non-spherical sinter first and then they are mixed together with non-spherical nut coke. From Figure 3-23 to Figure 3-26, it can be seen that the pressure drop decreases after mixing nut coke into an ore layer when the mixing ratio is less than 30 %. It indicates that adding nut coke into a sinter-pellet mixture layer has the ability to improve the permeability of a 2 layers charging packed bed. The best mixing ratio is 20 % and/or 30 % for reaching the lowest pressure drop.

Comparing the results of pellets, sinter and a mixture of pellets and sinter, it is concluded that they have similar performance when adding nut coke. It verifies that adding nut coke has the ability to improve the permeability of the blast furnace in the "dry zone" for different kinds of iron ores.



Figure 3-23 The effect of 10~15 mm nut coke on the pressure drop of mixing layer charging under different flow rates



Figure 3-25 The effect of 20~25 mm nut coke on the pressure drop of mixing layer charging under different flow rates



Figure 3-24 The effect of 10~15 mm nut coke on the pressure drop of mixing layers charging, flow rate 1 dm³/min



Figure 3-26 The effect of 20~25 mm nut coke on the pressure drop of mixing layers charging, flow rate 1 dm³/min

3.7 Multi-layers testing

A blast furnace is filled with alternating coke layers and ferrous materials layers. For maintaining the ascending gas through the burden column, it is desirable to have an optimum packed bed structure. The number of layers and the thickness of the layer are the most important factors for the permeability in the blast furnace. The gas ascending the furnace from the tuyeres to the furnace top is distributed mainly through the coke layer. To produce a path for gas flow through the furnace, a proper thickness of the coke layer has to be maintained. A multi-layer charging implies that there are many interfaces between coke layer and ore layer. These interfaces may influence the overall permeability of the blast furnace. Thus multilayers charging was tested to investigate the effect of number of layers under the same weight of coke and ore. Only pellets were tested in this case. The thickness of coke layer and ore layer are not totally comparable with an industrial blast furnace due to the limited dimension of the cold flow model in laboratory condition. The result just indicates the "unit cell" phenomenon in packed bed and it is applied to confirm the effect of multi-layers charging and explore the reason why the permeability of less layers is better than more layers based on laboratory conditions. Figure 3-27 demonstrates the pressure drop for different number of layers. From Figure 3-27 it can be seen that the pressure drop of 2 layers is smaller than that of 4 layers and that the pressure drop of 4 layers is smaller than that of 6 layers. The reason for the high resistance is caused by the low porosity in the interface which is demonstrated by the CT scanning described in in chapter 3.8.



Figure 3-27 Pressure drop of packed bed under different number of layers (Pellet mixing with 10 % 10~15mm nut coke)

3.8 Computerized Tomography scanning and image analysis

To further understand the effect of nut coke and number of layers on the permeability of a packed bed, a medical CT scanner (Figure 3-28) was used to investigate the physical structure of the packed bed with an ore layer and coke layer. The density of iron ore pellets is too high, making it very hard for a CT scanner to penetrate a pellet. Similar sized glass balls (12 mm) were used instead of spherical pellets (diameter range from 10~13 mm). Glass balls and nut coke are randomly packed in a barrel column. The height and diameter are 400 mm and 280 mm, respectively. The big sample of packed bed is put in the centre of the medical CT scanner.

During a computerized tomography (CT) scan, a thin x-ray beam rotates around an area of the body, generating a 3-D image of the internal structures



Figure 3-28 Schematic view of Medical CT Scanner

3.8.1 Brief introduction of CT scanner

The medical CT scanner used in this experiment is made by Siemens and the model is Siemens Somatom plus 4 Volume Zoom Scanner. An X-ray slice data is generated using an X-ray source that rotates around the object, X-ray sensors are positioned on the opposite side of the circle from the X-ray source. Digital geometry processing is used to generate a three-dimensional image of the inside of an object from a large series of two-dimensional X-ray images taken around a single axis of rotation. Once the scan data has been acquired, the data must be processed using a form of tomographic reconstruction, which produces a series of 2-D cross-sectional images [3]. Then a 3-D model will be constructed by post-process image analysis. A 3D analysis software Amira was adopted. The process is shown in Figure 3-29 and Figure 3-30.

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Figure 3-29 Schematic view of X-ray scanning [3]



3.8.2 Image analysis and results

Figure 3-31 is a 3-D reconstruction image of the coke layer. It consists of a series of 2-D cross-sectional images. Figure 3-32 is a vertical cross section of the 3-D coke-glass balls packed bed. Figure 3-33 shows top views of coke layer (A), interface (B) and glass ball layer (C). In Figure 3-33, the big grey particles are normal sized coke. The small white particles are glass balls. The black background is the porosity of the packed bed around coke and glass ball particles. Figure 3-33A shows the cross section of a coke layer in the packed bed. Coke particles are randomly packed in this layer and several small sized glass balls filled up the gaps of coke particles. This can also be observed from Figure 3-32. Figure 3-33B shows the interface between coke layer and glass ball layer. Many glass balls are arranged in the gaps of normal sized coke. The porosity of the interface decreases due to the glass in the gap among the big sized coke particles. This is the reason why the resistance of the interface is higher than that of the bulk coke layer. It also explains why the pressure drop of 2 layers is smaller than that of 4 layers and 6 layers. Figure 3-33C shows the cross section of the glass ball layer. Glass balls are randomly packed and make close contact with each other.

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Figure 3-31 3-D image of the coke layer



Figure 3-32 CT image of the cross section of 2 layers charging packed bed

Figure 3-34 shows the distribution of volume fraction of coke, glass balls and the void fraction along the height of the packed bed (top to bottom). The upper part is all glass balls and the lower part is the bulk coke layer. The percentage of glass balls is almost constant at the upper part in the glass balls layer (0 mm to 125 mm and the percentage goes down sharply along the height of packed bed from 125 mm to 200 mm. The height from 125 mm to 200 mm is defined as the transition layer between coke layer and glass balls layer. The porosity is

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determined by grey scales for each slide. The porosity of the transition layer is lower than that of the glass balls layer and coke layer. The minimum porosity is around 30 % in the transition layer.



Figure 3-33 Top view of coke layer, interface and glass balls layer in a 2 layers charging packed bed



Figure 3-34 Volume fraction change along the height of a packed bed

To investigate the effect of nut coke on the structure of an ore packed bed, a series of tests was conducted by a CT scanner with different mixing ratios. The packed beds of nut coke mixed with glass balls were scanned. The size of nut coke used in this experiment is 15~20 mm. Figure 3-35 and Figure 3-36 are the CT images under different nut coke mixing ratios(10 %, 20 % and 30 %).

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The small grey particle is the nut coke. The small white particles are glass balls and the background is void of the ore layer. When the mixing ratio increases, more and more nut coke appears in each layer of the whole packed bed. Some glass balls surround the big sized nut coke and generate larger porosity around the coke particle compared with only glass balls contacting with each other. This is the main reason for the porosity increase.



Figure 3-35 Top view of mixing ratio 10 % (A), 20 % (B) and 30 % (C)



Figure 3-36 Right view of mixing ratio 10 % (A), 20 % (B) and 30 % (C)

Figure 3-37 indicates the obtained porosity from image analysis based on the software Amira [4]. The height of the packed bed (column) is 200 mm. The bottom of the sample bed is set as 0 mm and the top is set as 200 mm. The porosity below 50 mm and the porosity above 185 mm are not reliable due to the effect of loose packing pattern. The determined porosity profiles demonstrate that the porosity in the packed bed mixed with 30 % nut coke is slightly larger than the bed mixed with 20 % and 10 % nut coke. It is difficult to quantify with an accurate value due to the fluctuation of the curve. The trend matches with the calculated porosity shown in Table 3-10. It proves that mixing 15~20 mm nut coke into a glass-ball layer could increase the porosity again and will lead to improved permeability.



Figure 3-37 Porosity of glass-ball packed bed with 10 %, 20 % and 30 % nut coke

3.9 Three layers pressure drop model

Based on the cold flow model experiments and CT images analysis, a three layers model was developed to evaluate the pressure drop when adding nut coke into an ore layer. Figure 3-38 shows the concept of the three layers model. It is a "unit cell" in the upper part of the blast furnace consisting of one ore layer and one coke layer. The pressure drop of the transition layer between ore layer and coke layer is also calculated and contributes to the total pressure drop of a unit cell.



Figure 3-38 The concept of the three layers model

The calculation of the total pressure drop is shown in Equations (3-2) - (3-5). It is the sum of three individual components: one ore - nut coke layer, one transition layer and one coke layer. The pressure drop in the ore layer and transition layer are calculated based on the friction factor from the Jeschar formula [1] shown in Equation (3-6) and Equation (3-7). The pressure drop in the coke layer is calculated based on the Ergun equation shown in Equation (3-8). The porosity and the thickness of each layer are determined by cold flow model experiments. The Jeschar formula is normally used to calculate the friction factor of a gas flow in a muliti-granular packed bed and the void fractions of each sized particles are considered in the Jeschar formula.

$$\Delta P_T = \Delta P_{Ore} + \Delta P_{Tra} + \Delta P_{Coke} \tag{3-2}$$

$$\Delta P_{ore} = f_{ore} \frac{\rho U^2 (1 - \varepsilon_{ore})}{D_{ore} \varepsilon_{ore}^3} \times H_{ore}$$
(3-3)

$$\Delta P_{tra} = f_{tra} \frac{\rho U^2 (1 - \varepsilon_{tra})}{D_{tra} \varepsilon_{tra}^3} \times H_{tra}$$
(3-4)

$$\Delta P_{coke} = f_{coke} \frac{\rho U^2 (1 - \varepsilon_{coke})}{D_{coke} \varepsilon_{coke}^3} \times H_{coke}$$
(3-5)

(1) The friction factors for Equations (3-4), (3-5) and (3-6) are described in the following:

$$f_{ore} = \left(\frac{160}{Re_{ore}'} + \frac{3.1}{Re_{ore}'^{(0,1)}}\right) \left(\frac{V_{nc}}{V_{ore}}\right)^{0.75}$$
 Jeschar equation (3-6)

$$f_{tra} = \left(\frac{160}{Re_{tra}'} + \frac{3.1}{Re_{tra}'^{(0,1)}}\right) \left(\frac{V_{ore}}{V_{coke}}\right)^{0.75} \quad \text{Jeschar equation}$$
(3-7)

$$f_{coke} = 1.75 + 150/Re'_{coke}$$
 Ergun equation (3-8)

Where,

$$Re'_{i} = \frac{\rho_{0}UD_{i}}{\mu(1-\varepsilon_{i})}, i = ore, transition \ layer, coke$$
(3-9)

(2) The average hydraulic diameters of each layer are given as below:

$$D_{i} = 1 / \sum_{n = ore, nut \ coke, \ coke} \frac{V_{n}}{V_{t} \cdot d_{n} \cdot \phi_{n}}$$
(3-10)

where,

ΔP_T	 Pressure drop of total packet 	ed bed, Pa/m
ΔP_{Ore}	: Pressure drop of ore-nut col	<mark>ke mixed layer</mark> , Pa/m
ΔP_{Tra}	Pressure drop of transition la	ayer, Pa/m
ΔP_{Coke}	Pressure drop of coke layer	, Pa/m
f _{ore}	: Friction factor of ore-nut cok	ke mixed layer
f _{tra}	 Friction factor of transition la 	ayer
f_{coke}	: Friction factor of coke layer	
H_{ore}	: The height of ore-nut coke r	nixed layer, m
H _{tra}	: The height of transition laye	r, m
H _{coke}	The height of coke layer, m	
V_{nc}	: Void fraction of nut coke	
Vore	: Void fraction of ore	
V _{coke}	: Void fraction of coke	
V_n	: Volume of coke, ore and nut	t coke, m^3
V_t	: Total volume, m^3	
d_n	Diameter of particle, m	
ϕ_n	Shape factor	

Figure 3-39 shows the comparison of calculated model case for pellet and experimental results. The size of nut coke is 20~25 mm for model calculation and experiments. The size of pellet is 12 mm and 10~13 mm for model and experiments, respectively. The results show that the curve of experiment almost fits with the calculated curve. It proves that the model could be used to calculate the pressure drop for a "unit cell" packed bed. The calculated result indicates that the pressure drop of 40 % nut coke mixing ratio is higher than the experimental data.



Figure 3-39 Comparison of model and experiment (gas flow rate at 1 dm³/min)

Figure 3-40 shows the calculated pressure drop for different mixing ratios under different gas flow rates. The pressure drop goes up with increasing gas flow rate. The curve of pressure drop shifts downward when adding 10 % nut coke into the ore layer. When adding more nut coke, 20 % and 30 % into the ore layer, the curve just shifts down slightly compared to 10 % nut coke. When adding 40 % nut coke, the pressure curve shifts up compared with 30 % nut coke. The model results show a similar phenomenon with experimental results. The optimum mixing ratio is 30 % for two layers "unit cell" structure. The trend of calculated results match with experimental results of 2 layers charging. The absolute value is not close enough and the model is worth to be further developed in future.

	Table 3-11	Parameters	of three I	ayers	mode
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	Value	Unit
$ ho_g$	1.205	kg/m^3
U	0.24	m/s
μ_g	17.7	$Pa \cdot S$
ϕ_{ore}	0.92	-
ϕ_{coke}	0.72	-
H_i	Measured	m
ε _i	Table 3-9	-



Figure 3-40 Calculated pressure drop based on the three layers model (Pellet: 10~15mm, Nut coke size: 20~25mm)

3.10 Summary

Cold flow model experiments show that by mixing nut coke into different ore layers the pressure drop is decreased. It indicates that nut coke has the ability to improve the permeability of the blast furnace. It is found that 10~15 mm, 15~20 mm, 20~25 mm, and 25~30 mm nut coke have the ability to improve the permeability of the packed bed including pellet, sinter and the mixture of pellet and sinter. For most cases, the best permeability is achieved when the mixing ratio is 20 % or 30 %.

One layer testing indicates that the pressure drop goes down with the increase of the nut coke mixing ratio. Adding nut coke will improve the permeability of the ore layer and more nut coke will generate better permeability as long as the mixing ratio is less than 40 %. The size of 10~15 mm nut coke is better than other size ranges (15~20 mm, 20~25 mm and 25~30 mm) to obtain a lower pressure drop under this experimental condition. Calculated and measured results indicate that the porosity increases with the increase of nut coke mixing ratio for each sized nut coke except for the 25~30 mm nut coke. For the case of 25~30 mm sized nut coke, the porosity increases when adding 10 % and 20 % nut coke, while the porosity decreases when adding 30 % and 40 % nut coke into ferrous burden. The explanation is that small particles (pellet) fill in the gap of big particles (nut coke) when the mixing ratio is higher than 30 %. It reduces the porosity of the mixture bed.

For two layers testing the pressure drop goes down when the mixing ratio changes from 0 % to 20 %. It goes up when the mixing ratio changes from 20 % to 40 %. The optimum mixing ratio is 20 % and/or 30 % (depending on nut coke size) for two layers charging. The differences between the one layer testing and two layer testing prove that the thickness of the coke layer has a significant influence on the permeability when adding nut coke in an iron ore layer. A balance between adding nut coke and keeping a proper thickness of the coke layer has to be established. Through a series of tests the best balance is obtained and the optimum mixing ratio is 20 % and/or 30 % to achieve the best permeability under laboratory conditions.

Comparing the results of pellet, sinter and their mixtures, it is concluded that they have similar performance for improving permeability when adding nut coke into ferrous burden.

Multi-layers testing shows that the pressure drop of 2 layers is lower than that of 4 layers and 6 layers and that the pressure drop of 4 layers is lower than that of 6 layers. CT image analysis reveals that many glass balls fill the gaps in the layer of normal sized coke. The porosity of the transition layer decreases because the glass balls filled in the gaps around the big sized coke particles. The minimum porosity is around 30 % in the interface. That is why the resistance of the interface

or transition layer is higher than that of the normal coke layer. The porosity curves demonstrate that the porosity in a packed bed mixed with 30 % nut coke is larger than the glass balls mixed with 20 % and 10 % nut coke. The trend matches with calculated porosity and measured porosity.

The results from a multi-layer prediction model show a good similarity with the experimental results. The optimum mixing ratio is 30 % for a two layers "unit cell" structure. However, there is still significant difference when comparing the absolute figures.

The experimental results and the detailed analysis prove that the cold flow model can provide useful information for understanding the optimum mixing ratio of nut coke under cold conditions, and for designing a high temperature experimental plan. Based on the cold flow model results, a nut coke mixing ratio of 20 % was applied in the high temperature experiments.

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4. HIGH TEMPERATURE EXPERIMENTS

4.1 Introduction

The laboratory equipment used for this research is developed to study the high temperature phenomena occurring in the burden of the blast furnace. Fundamental studies aim to increase the knowledge of the complex process of reduction, softening and melting and permeability of the burden in the blast furnace under the condition of mixing nut coke into an ore layer. The laboratory studies include the investigation of the influence of nut coke mixing ratio and nut coke size under different reducing conditions. To describe the processes of reduction and melting of burden materials, a large series of experiments are interrupted at different stages of the reduction. Obtained materials are studied by XRD, XRF and SEM-BSE-EDS.

4.2 Reduction, softening and melting experimental apparatus (RSM)

RSM is the name given to the Reduction and Softening and Melting Experimental Apparatus. It is developed at TU Delft based on the technical support from Tata Steel (IJmuiden) and financial support from the Materials innovation institute M2i. This equipment aims to investigate reduction kinetic characteristics and softening and melting behaviour during the reduction process of iron ore burden materials. During the RSM testing, temperature and gas profiles can be altered with time to simulate specific blast furnace conditions. Throughout the test, several parameters are measured (Table 4-1) to evaluate the test results.

Measurement parameters	Unit	Range
Time	min	-
Pressure drop	Pa	0~6000
Displacement	mm	0~100
Load on sample	kg	0.98 kg/cm ²
Mass flow $(N_2, CO, CO_2 \text{ and } H_2)$	NL/min	0~7.5
Gas analysis (CO, CO ₂ , H_2 and H_2O)	Vol. %	0~50
Sample temperature	°C	20~1550
Furnace temperature	O°	20~1600

Table 4-1	Summary	of the	RSM	measurements
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Figure 4-1 is a schematic representation of the newly constructed RSM apparatus. The furnace is heated by six heating elements regulated by a temperature controller that reacts on the furnace temperature measurement performed by a thermocouple in the furnace. Since the sample is heated by the heating elements around the outside of furnace tube, there is a differential temperature between furnace tube and sample bed. Therefore, a specific thermocouple is placed directly on the top of the sample bed to measure the actual sample temperature.

In the schematic overview of the RSM apparatus (Figure 4-1) gases (N_2 , CO, CO₂ and H_2) flow through mass flow controllers (MFC) to a gas mixing and heating chamber. The MFC are computer controlled and regulate the composition and amount of reducing gas. From the mixing chamber, the gas flows into a pre-heat furnace and then passes through the sample bed in the main furnace. The gas leaves the furnace through the off-gas pipe. The off-gas pipe is connected to a gas analyser which is used to analyse the composition of the mixing gas and the data is continuously logged by the computer. A filter is used to clean the dust before going to the gas analysers. The analysed gas is finally led to the ventilation hood. Through two other pipes, one before and one after the sample, the combined pressure drop, over the packed bed, is measured by a pressure sensor and logged by the computer. During the reduction and melting of the ferrous sample, the blast furnace burden materials become more compact. This contraction of the sample in the RSM apparatus is measured by a displacement sensor. This signal is also logged by the computer. Finally, water cooling flanges at the top and bottom of the furnace tube prevent damage to the rubber O-ring that seals the furnace.

The maximum temperature is 1550 °C in the centre of the furnace. Iron ore mixed with coke is filled in the crucible. There is a sample collector on the bottom of the furnace for collecting the molten iron and slag samples. There are 12 cups in the slag collector. The sample status can be observed and recorded by a video camera through glass viewports.

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Figure 4-1 RSM Experimental system sketch

RSM Components

In the following section, a description is given of the crucible, loading, sample collector, support jack, displacement sensor, differential pressure sensor, gas analyser, thermocouple, gas mixing and pre-heating station, datalogger and computer.

Crucible: The crucible is made of high grade graphite. Dimensions of the crucible holder are 64 mm inner diameter and an total height of 320 mm. It is shown in Figure 4-2. There are seven holes distributed over the bottom of the crucible to allow for dripping of molten slag and iron.



Figure 4-2 Drawing of the crucible

Loading: A static load is applied to the sample. This corresponds roughly to the weight of the overlying burden at the start of the cohesive zone.

Sample collector: It is used to collect the molten slag and iron. There is a plate which has 12 cups in the sample collector box (Figure 4-3). It can rotate 360° by hand. Two viewports are installed for monitoring the first and complete dripping moment.





Figure 4-3 Picture of sample collector

Support jack: Sample collector and balance locates on the support jack. It can ascend and descend freely by a hydraulic lever.

Displacement sensor: A displacement sensor is used to measure the sample burden contraction and expansion. The thermal contraction and expansion coefficient of the sample is defined as the rate of change of sample volume (a change in height of sample since the cross sectional area is fixed) with respect to the change in its temperature.

Differential pressure sensor: A differential pressure sensor is used to measure the pressure drop between the top and bottom of the sample bed. Pressure drop is the most important index of the burden permeability. From the pressure drop curve with temperature, the softening and melting temperature can be obtained.

Gas analyser: The gas analysis equipment shown in Figure 4-4 is used to analyse the gases exiting the furnace. Carbon monoxide, carbon dioxide and hydrogen and moisture are analysed with an error of 1 vol% of the total measuring range. Typical measurements vary between 0 and 50 % for each gas, which implies the error has a maximum of 0.5 vol%. The gas analysers are calibrated before every test with a reference gas of known composition. After the calibration the entire system is flushed with nitrogen to remove the remaining reference gas.



Figure 4-4 Image of gas analyser

Thermocouple: The thermocouple, B-type, is placed near the top of the sample bed. The operating range of this thermocouple is between 0 °C and 1800 °C with a higher accuracy than the standard K-type and S-type.

Gas mixing and pre-heating station: It consists of four parts, four gas cylinders, four mass flow controllers, one mixing chamber and one pre-heat furnace. Gas stored in gas cylinders and gas flow rate is controlled by a mass flow controller. The gases CO, CO_2 , H_2 , and N_2 are mixed in the mixing chamber. The mass flow controller (MFC) is calibrated to control a specific type of gas at a particular range of flow rates. The MFC has an inlet port, an outlet port, a mass flow sensor and a proportional control valve. The MFC is fitted with a closed loop control system which is given an input signal that is compared to the value from the mass flow sensor and adjusts the proportional valve. The flow rate is specified as a percentage of its calibrated full scale flow and is supplied to the MFC as a voltage signal. The accuracy of the MFC is 100 dm³ at atmospheric conditions. Mixing gas is pre-heated in the pre-heat furnace. Heated gas will flow into the furnace tube.

Datalogger: An ATM-05 datalogger is used in this system. It is an advanced 16 channels data recorder with extensive warning capabilities. A transducer with an active output (for example, temperature, humidity, pressure and voltage measurements) can easily be connected on a mA input or Volt input. It is connected to the computer to record all the data in the experimental process.

Balance: Balance is used to measure the sample weight change during the experiment process. The measure range is 0~61kg and accuracy is 0.1g. From top to bottom, the following parts put their weight on the balance: Loading, displacement bar, alumina support tube, graphite crucible, nozzle, bottom flange and slag collector.

Computer: The computer is the control centre for the whole test system. The datalogger is connected to the computer through USB2.0. MFC and balance are connected to the computer by a RS232 cable.

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Figure 4-5 Schematic view (left) and photograph (right) of the RSM apparatus

4.3 High temperature experiments

4.3.1 Materials

The iron ore used in this study is commercial pellet and sinter supplied. Table 4-2 and 4-3 shows the initial chemical composition (XRF analysis) of the sinter and pellet used in this study. Table 4-4 shows the initial chemical composition of the nut coke. XRD analysis results of pellet and sinter are shown in Figure 4-6 and 4-7. The pellet is composed of two main phases, hematite and quartz. The sinter is composed of two main phases, magnetite and iron silicon oxide. The size of pellet is between 10~13 mm, the size of sinter is between 10~15 mm.

Table 4-2 Chemical analysis of the pelle	et (wt%)
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Fe	SiO ₂	CaO	AI_2O_3	MgO	MnO	S	Р	TiO ₂	V_2O_5	Na ₂ O	K ₂ O	ZnO
64.4	4.5	0.22	1.2	1.2	0.37	0.007	0.042	0.2	0.037	0.06	0.024	0.23

Table 4-3 Chemical analysis of the sinter (wt%)

Fe	SiO ₂	CaO	Al ₂ O ₃	MaO	MnO	S	Р	TiO ₂	V205	Na ₂ O	K₂O	ZnO
									- 2 - 5			
57.4	3.6	12	0.65	0.66	0.46	0.061	0.039	0.1	0.02	0.03	0.064	0.01



Table 4-4 Chemical analysis of the nut coke



Figure 4-7 XRD phase analysis of sinter

4.3.2 Experimental conditions

To simulate the actual reducing conditions in the blast furnace, it is necessary to know what conditions occur in an industrial blast furnace. The most important parameters with respect to the behaviour of iron ore during the reduction process are as following:

- Temperature profile
- Gas profile (gas composition and gas flow rate)
- Loading profile

Experimental conditions found in literature [1-27] are roughly divided into four kinds of methods, classified by applied heating rate, gas composition, gas flow rate and load. The first method uses a constant heating rate and gas composition. The second method uses a constant heating rate and a varying gas composition. The third method uses a constant gas composition and a varying heating rate. The fourth method uses both varying heating rate and gas composition. Some investigators also applied load together with the above four methods. Some researchers do not use hydrogen in the mixing gas.

In this study, varying heating rate and gas composition, gas flow rate and constant load were applied in RSM testing. Four kinds of gases, CO, H_2 , CO₂ and N₂ were adopted. The size of sample and crucible were also sufficient to simulate industrial burden materials in the blast furnace.

4.3.2.1 Temperature profile

The temperature of gas in the blast furnace is reduced from 1750 $^{\circ}$ C in the bottom to 200 $^{\circ}$ C in the top in just a few seconds. However, the burden temperature increases from room temperature to 1500 $^{\circ}$ C in the tuyere level in hours [28]. Obviously, there is intensive heat exchange between the gas and the burden. This heat exchange can be described as following:

$$dQ = a \cdot F \cdot \Delta T \cdot d\tau \tag{4-1}$$

Where,

dQ	Heat transfer from gas to burden in time step $d au$

- *a* : Heat transfer coefficient
- *F* : Surface area of burden in contact with gas
- ΔT : Difference between gas and burden temperature, $\Delta T = T_{eas} T_{burden}$
- d au Time

A schematic picture of the solids and gas temperature profiles is shown in Figure 4-8. The blast furnace can be divided into three zones: upper heat exchange zone, middle heat exchange balance zone and lower heat exchange zone [29]. There exist large temperature differences between gas and burden in the upper and lower zone and the temperature in the lower zone is higher than in the upper. Therefore, intensive heat exchange occurs in the two zones. In the middle zone the value of the temperature difference is within 20 $^{\circ}$ C, and the heat exchange is modest. This zone is considered as the dynamic balance zone of gas and burden heat exchange and known as the thermal reserve zone.



Figure 4-8 Burden temperature estimated from observed gas temperature [29]

The selection of a temperature program for laboratory tests is, therefore, crucial in order to correctly simulate the reduction, softening and melting phenomena in the blast furnace. Table 4-5 below is the temperature profile based on ASAM (Tata Steel, IJmuiden) experiments which is used in this project.

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Temperature interval	Rate of temperature increase	Heating time
(°C)	(°C/min)	(min)
20-400	7	55
400-600	5	40
600-950	5	70
950-1050	1.2	83
1050-1550	5	100
1550-20	-5	306

Table 4-5 Temperature profile of RSM

4.3.2.2 Gas profile

Blast furnace gas ascends along the furnace through the burden layer and coke layer, and composition and temperature of the gas will change during this process.



Figure 4-9 Amount and composition of the ascending gas along the height of a blast furnace [29]

Figure 4-9 shows that gas composition changes during the process of gas ascending [29]. The CO content in the bottom part is between 35 % and 45 % and

the CO_2 is almost zero. In the furnace top, the CO content is between 20 % and 25 % and CO_2 content is between 15 % and 25 %. The total amount of CO and CO_2 is between 38 % and 42 %.

Different rates of reducing gas flow can result in a change of restrictive step in the reduction process. Therefore, sufficient gas – solid rate is needed to eliminate the effect of external mass transfer. An effective way to realize this demand is operation under a high speed of gas flow. Since high gas flow rates can cause longitudinal temperature gradients and increased operating costs, it is desirable to use the minimum gas flow rate necessary to achieve the specified gas velocity. Therefore, an experiment should be conducted to get a suitable value.

Table 4-6 below shows the gas profile based on ASAM that is used in this study.

Temperature (°C)	CO (%)	$H_{2}(\%)$	CO ₂ (%)	N ₂ (%)	Gas rate
20-250	0	0	0	100	0.005 dm ³ /min
250-600	25	4.5	20.5	50	
600-800	30	4.5	15.5	50	$0.015 dm^{3}/min$
800-1050	33	5	12	50	0.015 un /min
1050-1550	42	8	0	50	
1550-20	0	0	0	100	0.005 dm ³ /min

Table 4-6 Gas profile of RSM

After the maximum temperature has been reached the furnace is slowly cooled to room temperature while being purged with nitrogen at a rate of 0.005 dm³/min.

4.3.2.3 Load profile

The applied load during the reduction, softening and melting experiment should be decided from the industrial blast furnace at different temperatures and different positions. However, it is very difficult to measure the real stress in an industrial blast furnace. The stress distribution can be calculated by the Janssen equation [30] and Figure 4-10 shows the vertical stress in the blast furnace calculated by Kanayama et al. using Janssen theory [31].



Figure 4-10 Pressure and stress distribution in the blast furnace [31]

In the literature, a fixed load is normally used and the commonly applied loads are as follows: Kaushik [20], 0.98 kg/cm², Sternelandref [23], 0.2 kg~0.8 kg/cm², Nogueria[24], 0.98 kg/cm². The applied load in this study is fixed at 0.98 kg/cm².

4.3.3 Experimental plan

Table 4-8 shows the high temperature experimental schedule for this study which aims to investigate the effect and mechanism of nut coke mixing with ore on the performance of the blast furnace. Coke with dimensions <40 mm is used in this study. In a preliminary master's thesis study [1] pellet mixing with 0 %, 5 %, 10 % and 15 % nut coke (10~15 mm) were tested. Coke smaller than 10 mm strongly decreases the porosity of the packed bed, thus it is not adopted in this study. Coke with size 25~40 mm cannot be tested due to the limitation of the crucible size (64 mm diameter). This study mainly focuses on the effect of 10~15 mm nut coke on the performance of the blast furnace. Cold flow model experiments revealed that the nut coke mixing ratio of 20 %~30 % is the optimum parameter to obtain the best permeability. Thus, a nut coke mixing ratio of 20 % was tested to further study the effect and mechanism of nut coke on the reduction kinetics, softening and melting behaviour and permeability in the cohesive layer in high temperature experiments with the RSM set-up.

To study the mechanism of nut coke on the reduction process, experiments in a series are interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C. It aims to get an insight into the behaviour of reduction and softening and melting with a similar chemical composition and initial structure.

Table 4-7 Experimental plan

A series: Pellet mixing with nut coke
 Full range temperature profile (from 20 °C to 1550 °C)
• 0 % and 20 % nut coke
B series: Pellet mixing with nut coke
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 %)
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 %)
C series: Sinter mixing with nut coke
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 %)
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 %)
D series: Mixture of P+S mixing with nut coke
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 %)
 Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 %)

Figure 4-11 shows the charging pattern of ferrous materials and coke in the crucible. Top and bottom layers are coke layers. The middle layer consists of ferrous materials mixed with nut coke. All tests are conducted with an equal amount of ferrous material (500 g) and coke (95 g, calculated based on a coke rate of 300 kg/THM). The thickness of the coke layer decreases with an increase of the nut coke mixing ratio.



Figure 4-11 Schematic view of the sample bed in the crucible

4.3.4 Experimental procedure

All tests were conducted with an equal amount of ferrous material and coke. The ferrous materials and coke are selected and weighed to simulate the coke ratio in an industrial blast furnace. All samples were dried at 105 $^{\circ}$ C in a dry furnace for

24 h to ensure complete removal of the moisture. Before the start of heating up the furnace, N₂ is introduced to the furnace with 0.005 dm³/min to exhaust the air in furnace. Then the connection of gas tube is checked to make sure no leakage of furnace system and gas analyser takes place. The working temperature starts from 20 °C to 1550 °C with varying heating rate. The total flow rate is 0.015 dm³/min consisting of CO, H₂, CO₂ and N₂ with varying gas composition with time.

During the reduction, softening and melting testing, differential pressure across the sample bed, contraction of sample bed, and the temperature of the sample bed were continuously measured and recorded at 5 s interval time. The composition of the off-gas is measured and recorded by a gas analyser at interval times of 20 s. Based on the oxygen and carbon balance, the reduction degree of ferrous materials was calculated according to Equations 4-2~4-7 in Chapter 4.4.1.

The molten samples of slag and iron were collected by a sample collector with 12 cups. Samples were examined by XRF, XRD and SEM-EDS. To better understand the characteristics of reduction, softening and melting at different temperatures, a series of interrupted tests were done. When the temperature of sample reaches the pre-set value, gas supply and power supply are immediately stopped. Nitrogen gas (0.005 dm³/min) was introduced to the furnace to cool down the furnace and to discharge the reducing gas as soon as possible. The sample was taken out when the temperature reached room temperature. Liquid resin was injected into the crucible to fix the sample bed and keep the original structure of the packed bed. The crucible was cut into two pieces after solidification of the resin. After polishing the cross section of the sample bed was examined by XRF, XRD and SEM-DES. Also the structure of the sample bed is studied by image analysis processing.

4.4 Data interpretation

4.4.1 Reduction characteristics

A common way to represent reducibility is to plot the oxygen to iron ratio (O/Fe, reduction degree) as a function of temperature and time. The initial amount of oxygen and iron is calculated based on the chemical composition of the iron ore.

4.4.1.1 Calculation of oxygen removal

The reduction degree, R (%), was calculated according to the following definition:

$$R(\%) = \frac{m_{O,Rem}^{Acc}}{m_{O,Ori}} \times 100 \%$$
(4-2)

where,

 $m_{0,Rem}^{Acc}$: Accumulated mass of oxygen removed from the sample (g)

 $m_{0.0ri}$: Original content of oxygen present as iron oxides (g)

Method A (based on gas analyser): One way to calculate *R* is to use the oxygen content change in the gases between the inlet and outlet of the reactor system (conversion of CO to CO_2 and/or H_2 to H_2O). However, the reduction degree calculated through this method may not be very accurate due to the need of accurately known gas volumes at gas inlet and outlet. It will also include other metal oxide reduction products if other oxides are present in the ore such as MnO and TiO₂.

The oxygen removal due to reduction can then be calculated as:

$$\dot{m}_{0.Rem} = \dot{m}_{0.0utlet} - \dot{m}_{0.Inlet} \tag{4-3}$$

For a reducing gas mixture containing hydrogen the oxygen removal in the form of H_2O must also be taken into account in Equation 4-3.

$$\dot{m}_{O.Rem} = \begin{pmatrix} \frac{[\%CO]^{outlet} + 2[\%CO_2]^{outlet} + [\%H_2O]^{outlet}}{[\%N_2]^{outlet}} \\ -\frac{[\%CO]^{inlet} + 2[\%CO_2]^{inlet} + [\%H_2O]^{inlet}}{[\%N_2]^{inlet}} \end{pmatrix} \times \frac{\theta_{N2} \times M_O}{V_O}$$
(4-4)

where

[%i]	:	Volume of percentage of species i
θ_{N_2}	:	Volume flow of N ₂ , dm ³ /min /s
M_0^2	:	Molar mass of oxygen, g/mol
V_0	:	The standard volume of an ideal gas at room temperature, dm ³ /mol

The mass of oxygen removal can now be calculated by integrating the removal rate over time:

$$m_{O,Rem} = \int_0^t (\dot{m}_{O,Rem}) \times dt \tag{4-5}$$

During a time increment with constant oxygen removal rate, the solution to the integral in Equation 4-5 is simply the product of the oxygen removal rate, $\dot{m}_{0.Rem}$, and the time, *t*, of the increment under consideration:

$$m_{0,Rem} = \dot{m}_{0,Rem} \times t \tag{4-6}$$

The accumulated oxygen removal, finally, is calculated by summing up the mass of oxygen removal for each time increment (t_i) :

$$m_{0,Rem}^{Acc} = \sum_{i=1}^{T} (m_{0,Remi} \times t_i)$$
(4-7)

where T is the total number of time increments.

Method B (based on quenching experiment): This way is to weigh and analyse the interrupted samples from different temperatures by separating the coke particles from the ferrous materials (reduced metal plus any remaining oxides). All metal and remaining ferrous materials can be collected, weighed and chemically analysed. This method will produce the most reliable results for the reduction degree.

Method A is adopted as the main way to calculate the reduction degree. Method B is an assistant approach to calculate the reduction degree and calibrate the results of method A.

4.4.1.2 Mass balance of carbon

Similarly to the oxygen removal calculation the extent of the solution loss reaction, i.e. carbon deposition at low and carbon consumption at high temperatures, respectively, can be calculated by a mass balance of carbon. Thus, the rate of carbon loss can be expressed as:

$$\dot{m}_{C.Loss} = \dot{m}_{C.inlet} - \dot{m}_{C.outlet} \\ = \begin{pmatrix} \frac{[\% CO]^{inlet} + [\% CO_2]^{inlet}}{[\% N_2]^{inlet}} \\ -\frac{[\% CO]^{outlet} + [\% CO_2]^{outlet}}{[\% N_2]^{outlet}} \end{pmatrix} \times \frac{\theta_{N2} \times M_C}{V_O}$$
(4-8)

where

 C_0 : Molar mass of oxygen, g/mol

Carbon loss is then at all times given by integration of the removal rate over time:

$$m_{C,Loss} = \int_0^t (\dot{m}_{C,Loss}) \times dt \tag{4-9}$$

For time increments of constant carbon deposition rate, the accumulated carbon deposition is given by summing up all time increments, similar to Equation 4-7 for oxygen removal:

$$m_{C,Loss}^{Acc}(t) = \sum_{i=1}^{T} (m_{C,Lossi} \times t_i)$$
(4-10)

where a positive value represents carbon deposition and, consequently, negative values represent carbon consumption.

4.4.2 Softening and melting (S&M) behaviour

The softening and melting temperatures are defined as the point of inclination of the pressure drop curve and sample contraction curve.

 $T_{\text{Softening}}$ is defined as the starting softening temperature of the ore particles. For this study this point is defined as the temperature where the pressure drop over the sample increases more than 5 %, compared to 20 measurements counted backwards.

For the point of inclination holds:

$$\frac{\Delta P_t - \Delta P_{t-20}}{\Delta P_t} > 1.05 \tag{4-11}$$

For the contraction curve, the softening temperature is the point of the common tangent of the shrinking and the softening sections of the displacement curve [25]. The contraction curve is the result of the relative movement of the displacement sensor as a function of temperature. The movement itself is the result of the collapse of the structure of the iron ore particles due to the load on the sample and the softening and melting effect of the hot gas.

 $T_{Melting}$ is defined as the temperature at the maximum value of the pressure drop curve. For the contraction curve, the meltdown temperature is the point of the common tangent of both softening and meltdown sections of the displacement curve. At that temperature the permeability will reach a minimum after which it will start to recover. The recovery is the result from melt dripping from the void and consequently the emptying of the void fraction thus lowering the pressure drop over the sample. Because a sample collector with two view ports seats at the bottom of the furnace in this study, it is possible to observe molten metallic iron and slag dripping into the sample collector. By comparison of the dripping time with the temperature curve, the dripping temperature can be determined. Then the melting temperature achieved from three methods can be compared and validated with each other.

4.4.3 Permeability

The surface under the pressure drop curve is a measure for the resistance against the gas flow. Bos [1] used the S1 and S2 values to represent the permeability with the total surface area under the pressure drop curve as shown in Figure 4-12. A

lower S value denotes a better permeability. A refinement is made between the S1 and S2 value. When the RSM reaches the temperature of 1500 °C, partial and temporary blocking of the nozzle may interfere with the pressure drop curve and potentially making a correct calculation of the resistance to the gas flow more difficult. To overcome this effect the S2 value only looks at the left hand side of the pressure drop curve which is less prone to variations in pressure drop since it is calculated at lower temperatures and at slower contraction rates.



Figure 4-12 Surface calculation for S1 value (left) and S2 value (right) [1]

4.4.4 Sample analysis

Weight analysis: The sample (iron ore and coke), crucible and sample cups are weighed, respectively, before and after each experiment. The total weight loss of oxygen and coke are determined in this way.

Structure of the packed bed (interrupted experiments): N_2 was used to cool down the crucible temperature and discharge the reducing gas. When the crucible reaches room temperature, it was taken out from the furnace. The structure of the sample should be kept as close to the high temperature state as possible. Liquid resin was injected in the crucible for fixing the iron ore, remained coke particles and slag. After liquid resin solidification the crucible was cut and the cross section of the packed bed was scanned. The scanned picture was used to study the structure of the packed bed. The samples were analysed with XRF, XRD and SEM-BSE-EDS and the micro-structure, chemical characterization and phase transformation were investigated.

Collected samples of metallic iron and slag: The reduction products (metallic iron and slag) were collected during the experiment in the sample collector with 12 cups. The collected intermediate samples (initial, midterm and final) were analysed with XRF, XRD and SEM-EDX to investigate the chemical and mineralogical changes related to the effect of nut coke.

Gas analysis: Gas samples generated during the experiment were collected through the gas outlet at the furnace top. A gas analyser was applied to analyse the gas composition continuously as function of time.

4.4.5 Data analysis and expected results

Reduction characteristics: Based on the data of the gas analyser, the reduction degree and carbon loss as a function of time and temperature were plotted as shown in 5.4.1. The variation of CO, CO_2 , H_2 , and H_2O gas during reduction of iron ore were also plotted as a function of time and temperature. The reduction characteristics could be achieved by this way Based on the XRF, XRD and SEM-EDX, the mechanism and fundamentals for these characteristics were revealed.

Softening and melting behaviour: Based on displacement curve and pressure drop curve as a function of temperature, the basic information of softening and melting, such as softening temperature and dripping temperature were achieved. The properties of softening and melting are controlled by reduction degree, slag basicity, amount of gangue and flux, phase chemistry and their distribution in the micro-structure. The effect of nut coke on the above mentioned phenomena was investigated. Based on softening and melting information related with SEM-EDS pictures and sample bed structure, the mechanism and fundamentals of the effect of nut coke on the softening and melting behaviour were revealed.

Permeability: The figure of pressure drop as a function of time and temperature is the best way to show the permeability of a sample bed. Permeability depends on the porosity and micro and macro structure of the sample bed. It is also influenced by softening and melting behaviour in the cohesive zone. The analysis of softening and melting behaviour is very important information for the permeability study. The mechanism and fundamentals of permeability were revealed by the pressure drop figures related with pictures of scanning and SEM-EDS of the sample bed.
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5. HIGH TEMPERATURE EXPERIMENTS: RESULTS AND DISCUSSION

The high temperature experiments were conducted to study the behaviour of ferrous burden with coke under a simulated blast furnace gas and temperature profiles. The gas and temperature profiles are referenced from ASAM used at Tata Steel in IJmuiden. Two types of experiments were performed at high temperatures: (1) full temperature profile experiments (20 - 1550 °C) and (2) interrupted experiments at different temperatures, as described in chapter 4 and listed below.

A series: Full temperature range experiments

- Case 1: Coke layer ore (pellet) layer coke layer (without nut coke, 0 %)
- Case 2: Coke layer ore (pellet) & nut coke mixing layer coke layer (with • nut coke, 20 %)

Interrupted experiments were conducted to study the influence of nut coke at different stage of reduction and softening and melting. It is expected to better understand the behaviour and mechanism under the effect of nut coke. Three series experiments were tested:

B series: Pellet mixing with nut coke

- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 % nut coke)
- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 % nut coke) •

C series: Sinter mixing with nut coke

- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 % nut coke)
- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 % nut coke)

D series: P+S (pellet+sinter) mixing with nut coke

- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (0 % nut coke) •
- Interrupted at 900 °C, 1100 °C, 1300 °C and 1400 °C (20 % nut coke)

5.1 Benchmarking experiments and reproducibility testing

The crucible used in the RSM is made of high grade graphite. Graphite is a kind of material that can endure high temperatures in a reducing atmosphere. But it could react with CO₂ gas through the Boudouard reaction and generate CO gas. To minimise this effect, a high grade graphite with high density and low porosity was selected to make the crucibles for the RSM experiments.

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Two coke layers (one layer on top of the ore layer and the other layer below the ore layer) were used to simulate the industrial blast furnace charging pattern. This thesis mainly focuses on the effect of nut coke on the behaviour of ferrous burden (pellet, sinter, or their mixture) at elevated temperatures.

The benchmarking experiments were conducted to verify the effect of the coke layers above and below the ferrous burden on the experimental results under the conditions of mixing nut coke with an ore layer. Figure 5-1 shows the charging pattern adopted in the benchmarking experiments. Benchmarking Case 1 is the normal charging pattern used in this thesis. In Benchmarking case 2, ceramic balls are used to replace the coke layers in case 1 to check if there are any differences in the burden behaviour.



Benchmarking Case 1 Benchmarking Case 2



The Benchmarking experiments were conducted with a specific gas profile and temperature profile as shown in Figure 5-2. The incoming-gas composition of CO and CO₂ are set to 33 vol% and 12 vol%, respectively, shown by the two blue lines. The temperature range is set between 950 °C and 1200 °C when reacting gas mixture is switched on. The green curve and black curve show the off-gas of CO for case 1 and case 2, respectively. It can be seen from Figure 5-2 that the off-gas curves of CO have little difference between case 1 and case 2. It seems that there is some influence on the off-gas profile when using a coke layer above and below the ore layer in the crucible. To gain further information, a mass balance analysis was conducted. Table 6-1 shows the mass balance before and after the testing. Mass balance results show that all the carbon containing materials, including the graphite crucible, coke layer and nut coke, lose certain weight during the experimental period. But they don't lead to the influence on the reduction of iron ore and the consumption of nut coke. Thus, charging method of benchmarking case 1 is selected in this study.





	Materials	Case 1 (g)	Case 2 (g)
	Crucible	931.82	926.62
	Pellet	501.32	501.07
Before testing	Nut coke	19.56	20.72
	Coke layer	76.80	Ceramic
	Total	1529.50	1808.32
	Crucible	919.34	906.83
	Pellet	426.55	426.59
After testing	Nut coke	14.25	15.20
-	Coke layer	74.57	0
	Total	1434.71	1708.56
	Crucible	12.48	19.76
	Pellet	74.77	74.48
Weight loss	Nut coke	5.31	5.52
	Coke layer	2.23	-
	Total	94.79	99.76
	Total carbon loss	20.02	25.42

Table 5-1 Mass balance analysis

The results of a series quenching testing at different temperatures were used to compare and to determine the reproducibility of high temperature experiments with the RSM system. The results show a good agreement with different cases, according to recorded the off-gas compositions. The off-gas curves for different cases almost overlap with one another and they just have a slight deviation as shown in Figure 5-3. Therefore the experiments can be considered to be well reproducible.



Figure 5-3 Off-gas profiles of four interrupted experiments (900 °C, 1100 °C, 1300 °C and 1400 °C) combined in one figure.

5.2 Reduction characteristics

5.2.1 Reduction degree

The reduction kinetics curves for pellet mixed with nut coke (interrupted at 1400 °C) are shown in Figure 5-4. The reduction degree of mixed charging (iron ore mixing with nut coke), is higher than the normal layer charging (iron ore without nut coke) from temperature 800 °C upward. There are several turning points on the reduction degree curves due to the change of heating rate and gas composition. The reduction degree increases very slowly after 1300 °C and almost approaches 100 %. The changed heating rate from 5 °C to 2.5 °C at 1300 °C is one of the

reasons for this phenomenon. The other reason is thought to be a small amount of residual iron oxide and slag in the centre of iron ore surrounded by the thick metallic iron layer at the last stage of the reduction process. The resistance is relatively high for gas diffusion in a thick metallic layer. It is difficult to further reduce the FeO at the same rate at this stage. After the collapse of pellet or sinter, the liquid phase flows out and directly makes contact with coke particles. The reduction degree will soon go up to 100 % by the direct reduction reaction ((FeO)+C=Fe+CO). The reduction curves almost overlap each other below 800 °C. The reduction kinetics curves for sinter mixed with nut coke demonstrate a similar trend with Figure 5-4. Thus, it is not shown and explained here.



Figure 5-4 Kinetics curves of reduction for pellet mixed with nut coke (Interrupted at 1400 °C)

It is known that below 800 °C the stability of CO_2 increases as the temperature decreases and thus the Boudouard reaction is limited. CO is stable above 900 °C and CO_2 produced from the reduction of iron oxide will be reduced back to CO by the Boudouard reaction. That could explain why the reduction degree of pellet mixed with nut coke is higher than pellet only when the temperature is above 800 °C. Thus, the Boudouard reaction (Equation 5-1), caused by the nut coke, is one of the reasons for enhancing the reduction degree. The assumption is verified by Figure 5-5 where it can be seen that the CO potential in the off-gas for the case of pellet mixed with nut coke is obviously higher than pellet only in the temperature range of 800 °C to 1400 °C. It is difficult to directly read from Figure 5-5. Thus, the

data extracted from Figure 5-5 is provided in Table 5-2 for easier comparison. Furthermore, the equilibrium CO composition is calculated based on thermodynamic data provided in Table 5-3 and also referred from Fe-O-CO equilibrium diagram.



Figure 5-5 The off-gas profiles of the pellet case

	Temperature	800	900	1000	1050	1100	1200	1300	1400
	(°C)								
	0% nut coke	53.0	64.3	73.1	76.2	83.2	89.8	96.8	99.0
$(0/(00+00_2))$	20% nut coke	53.4	65.1	73.9	77.3	83.8	90.3	97.5	99.3
(70)	Equilibrium	64.5	67.3	69.6	70.6	71.5	73.0	74.4	75.5

Table 5-2 CO potential of experiments and equilibrium

1	$Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$	$\log K_p = \frac{2726}{T} + 2.144$
2	$Fe_3O_4 + CO = 3FeO + CO_2$	$\log K_p = \frac{-1373}{T} - 0.341 \log T + 0.41$ $- 10^{-3}T + 2.303$
3	$\frac{1}{4}Fe_{3}O_{4} + CO = \frac{3}{4}Fe + CO_{2}$	$\log K_p = \frac{-2462}{T} - 0.99T$
4	$FeO + CO = Fe + CO_2$	$\log K_p = \frac{688}{T} - 0.9$

Table 5-3 Thermodynamic data of iron oxide reduction by CO [1]

Table 5-2 shows the CO potential of experiments for 0 % and 20 % nut coke and also the equilibrium CO composition. To make a clear view, the data of Table 5-2 are translated into Figure 5-6, where it can be seen that the CO potential of adding 20 % nut coke is slightly higher than that of 0 % nut coke. When the temperature is higher than 1000 °C, the CO potential of off-gas is higher than the equilibrium CO composition of FeO \rightarrow Fe reduction. The CO composition measured in the off-gas is assumed to be equal to the local CO potential in the crucible. It indicates that metallic iron could be produced from 1000 °C and above. The increased CO potential is the driving force for enhancing the reduction degree.



Figure 5-6 Fe-O-CO-H₂ equilibrium diagram [1]

5.2.2 Reduction rate

Figure 5-7 is the schematic view of the diffusion or reaction rates for different steps of iron ore reduction. It is drawn based on shrinking core model for iron oxide reduction with CO/H_2 gas. Three steps are expressed in Equations (5-2) through (5-4) [2]. Based on the reduction kinetics analysis, the reduction rate of iron oxide could be controlled by external diffusion in the gas boundary, internal diffusion through the solid product layer and also by the chemical reaction at the interface. From Equation 5-5 it can be concluded that the reduction rate of iron oxide depends on the resistance of three steps and on the driving force from bulk gas and the equilibrium CO/H_2 concentration.



Figure 5-7 Schematic view of rate controlling steps for iron oxide reduction with CO/H_2 gas

$$J_{A1} = 4\pi r_0^2 \cdot \beta_A (C_A^0 - C_A^s)$$
(5-2)

$$J_{A2} = \frac{4\pi r_0 r}{r_0 - r} \cdot D_{eff} (C_A{}^s - C_A{}^i)$$
(5-3)

$$R_{i} = 4\pi r_{i}^{2} \cdot k \left(C_{A}^{i} - \frac{C_{P}^{i}}{K} \right)$$
(5-4)

$$R_{A} = \frac{C_{A}^{0} - C_{A}^{*}}{\frac{1}{4\pi r_{0}^{2} \cdot \beta_{A}} + \frac{1}{(\frac{r_{0}r}{r_{0} - r}) \cdot 4\pi D_{eff}} + \frac{K}{1 + K} \frac{1}{4\pi r^{2} \cdot k}}$$
(5-5)

Where J_{A1} is external diffusion rate, J_{A2} is internal diffusion rate and R_i is the chemical reaction rate at the interface, R_A is the total reduction rate of iron ore reduction reaction. r_0 is the radius of single iron ore particle, r is the radius of the reaction interface, β_A is the gas diffusion coefficient in boundary, D_{eff} is the gas diffusion coefficient in the solid product layer, k is the reaction rate constant, K is

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the equilibrium constant, $C_A^{\ 0}$ is the concentration of reduction gas in bulk gas, $C_A^{\ s}$ is the concentration of reduction gas at the surface of iron ore, $C_A^{\ i}$ is the concentration of reduction gas at the reaction interface, $C_P^{\ i}$ is the concentration of the gas of product.

Figure 5-8 shows the reaction rate for the pellet case (Interrupted at 1400 °C). There are four stages divided by three incoming-gas changing moments at temperatures of 600 °C, 800 °C and 1050 °C, respectively. The reaction rate keeps going up with increasing temperature below 800 °C. Then the reaction rate goes down when the temperature becomes higher than 800 °C. The reaction rate of orenut coke mixed charging is higher than the standard charging without nut coke participation. The reaction rate goes down after 800 °C or 900 °C which could be explained by the reduction retardation [3]. The reaction rate is likely controlled by chemical reaction below 900 °C and controlled by gas diffusion when the temperature is above 900 °C. There is a dense metallic iron layer on the outer surface of iron ore pellet. The dense metallic iron layer results in a high resistance to the diffusion of reducing gas from outer layer to inner layer of iron ore pellet. Mousa et al. [3] confirmed this phenomenon in their study. The reaction rate of adding 20 % nut coke is higher than that of adding 0 % nut coke between 800~1300 °C. This is caused by the increased CO potential from nut coke presence that increases the driving force for the reduction reaction. Based on Equation (5-5), it will enhance the reduction rate.



Figure 5-8 The reduction rate of the pellet case (Interrupted at 1400 °C)

5.2.3 Sample analysis (SEM-BSE-EDS)

The samples collected from the crucible after quenching were analysed by SEM-EDS technique. ImageJ software was adopted to further quantify the area of each phase by Threshold (Grey level) [4]. Figure 5-9 shows the overview of the ImageJ software. It is a very smart and convenient tool for image analysis and statistics.



Figure 5-9 Overview of ImageJ [4]

Figure 5-10 shows the SEM-BSE-EDS images of the pellet quenched at 1100 °C. Figure 5-10A is the case of 0 % nut coke. EDS and XRD analysis indicates that it mainly consists of FeO, Fe₃O₄ and (Mg, Fe)₂SiO₄. Figure 5-10B is the case of 20 % nut coke. EDS and XRD analysis indicate that it mainly consists of Fe, FeO, and Fe₃O₄. The quantified area of each phase is listed in Table 5-4 according to ImageJ analysis process as shown in Figure 5-11. From Table 5-4, it can be seen that the area of Fe and FeO for the case of 20 % nut coke is larger than the 0 % nut coke case. The area of Fe₃O₄ for 20 % nut coke is smaller than 0 % nut coke. It indicates that the iron oxide reduction of 20 % nut coke is better than that of 0 % nut coke.

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Figure 5-10 SEM-BSE-EDS images of pellet (Quenched at 1100°C)



Figure 5-11 Image analysis by ImageJ software

Table 5-4 Area of each phase (Quenched at 1100 °C)

	Fe	FeO	Fe ₃ O ₄	(Mg,Fe) ₂ SiO ₄
0 % nut coke	6.1 %	38.82 %	54.29 %	0.79 %
20 % nut coke	17.8 %	40.34 %	41.78 %	0 %

Figure 5-12 shows the SEM-BSE-EDS images of the pellet quenched at 1400 °C. Figure 5-12A is the case of 0 % nut coke. EDS and XRD analysis indicates that it mainly consists of Fe, FeO, (Mg, Fe)₂SiO₄. Figure 5-12B is the case of 20 % nut coke. EDS and XRD analysis indicates that it mainly consists of Fe and (Mg, Fe)₂SiO₄. The area of each phase is quantified by the same method with Figure 5-12. The data are listed in Table 5-5. The area of Fe for 20 % nut coke is larger than that for 0 % nut coke. There is almost no FeO found in the case of 20 % nut coke. It also proves that the reducibility of the case 20 % nut coke is better than that of 0 % nut coke.

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Figure 5-12 SEM-EDS image of pellet (quenched at 1400 °C)

Table 5-5 Area of each phase (quenched at 1400 °C)

	Fe	FeO	(Mg,Fe) ₂ SiO ₄
A: 0 % nut coke	46.1 %	29.4 %	24.5 %
B:20 % nut coke	76.6 %	0 %	23.4 %

Through the SEM-BSE-EDS image analysis, it further verifies that the reduction behaviour could be improved by nut coke-ore mixed charging. It shows similar phenomena with reduction curves calculated based on incoming-gas and off-gas profiles.

5.3 The consumption of nut coke

The total carbon loss in the experimental system includes the loss of the graphite crucible, normal coke in the coke layers and the nut coke in the iron ore layer. This study focuses on the effect of nut coke, thus the consumption of nut coke in the iron ore layer needs to be quantified. Figure 5-13 is the schematic view of the charging method used in high temperature experiments. For the two cases the same graphite crucible, the same weight of iron ore and the same weight of total coke were used. The only difference is: for case 1 adding a 20 % nut coke into the ore layer and case 2 without adding nut coke in the ore layer. Based on Equation 5-6, the consumption of nut coke was calculated.

 $m_{nc,\,loss} = m_{C1,\,loss} - m_{C2,\,loss}$

(5-6)

Where $m_{nc, loss}$ is the weight loss of nut coke, $m_{C1, loss}$ is the total weight loss of carbon in case 1, $m_{C2, loss}$ is the total weight loss of carbon in case 2.

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The total carbon loss was calculated from the mass balance of carbon between the incoming-gas profile and off-gas profile as shown in Chapter 4.4.1.



Figure 5-13 Schematic view of charging method used in high temperature experiments





Figure 5-14 demonstrates the nut coke loss in nut coke-pellet mixed layer as a function of temperature. It can be seen that the loss of nut coke increases with temperature and almost 40 % nut coke is consumed in the reduction process under this condition. It proves that nut coke takes part in the possible reactions which are described below:

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Boudouard reaction:

 $C+CO_2=2CO$



Figure 5-15 Possible reactions caused by nut coke

Figure 5-15 is a schematic view of possible reactions with the nut coke in an orenut coke mixed charging layer. The Boudouard reaction as well as the water-gas reaction will have a significant influence on the nut coke consumption. It is necessary to clarify the mechanism of the two reactions.

Boudouard reaction

It is known that CO_2 is generated during the reduction process of iron ore by Equation 5-7. When the formed CO_2 encounters with nut coke in the ore-nut coke mixed layer, the new CO will be produced by the Boudouard reaction. The regenerated CO will react with iron oxide again as an extra reducing agent. Normally, the starting temperature of Boudouard reaction in the blast furnace is around 900 °C ~1000 °C [1].

$$Fe_xO_y+CO=Fe_{x-1}O_{y-1}+CO_2$$

Figure 5-16 is the Boudouard reaction equilibrium diagram. The figure is divided into two zones by the curve, the left zone is the CO decomposition zone and the

(5-7)

right zone is the CO formation zone. If the CO potential is in the right zone, it indicates that the Boudouard reaction proceeds from left to right. The obtained experimental data about the CO potential from the off-gas are plotted in Figure 5-16. The data show that the Boudouard reaction starts from around 700 °C. It proves that the Boudouard reaction occurred in this reaction system. On the other hand, it also proves that nut coke could reduce the starting temperature of the Boudouard reaction. However, Figure 5-14 indicates that the nut coke loss has already happened below 600 °C and above 400 °C. It could not be promoted by the Boudouard reaction. The water-gas reaction is the possible reason to explain the nut coke loss below 600 °C. Thus, water-gas reaction is discussed below.



Figure 5-16 Carbon gasification equilibrium diagram [2] with added experimental data od using or not using nut-coke.

Water-gas reaction

 H_2 was used as an additional reducing gas to simulate the industrial blast furnace in this study. H_2O is generated by the reaction of hydrogen with iron oxide (Equation 5-8). The formed H_2O could react with nut coke in the ore-nut coke mixed layer by the water-gas reaction. Similar to CO, the regenerated H_2 will participate in the reduction reaction again as an extra bonus.

$$Fe_{x}O_{y}+H_{2}=Fe_{x-1}O_{y-1}+H_{2}O$$

Y. Kashihara et al. [5] pointed out that presence of H_2 increases the carbon gasification rate when the temperature is below 1300 °C. Their experiment was

(5-8)

conducted under ore-nut coke mixed charging conditions. They concluded that the water-gas reaction contributed to an increase of the carbon gasification rate.

The starting temperature of the carbon gasification reaction (Equation 5-9) decreased when H_2 is mixed with CO as an extra reducing agent and the total nut coke consumption rate increased. The lower starting temperature of the carbon gasification is caused by the lower starting temperature of the water-gas reaction compared with the Boudouard reaction [5]. The theoretical starting temperature of the water-gas reaction is 667 °C calculated from Equation 5-9 [2]. Y. Kashihara stated that the starting temperature of the water-gas reaction could be reduced by nut coke. This could explain the nut coke loss below 600 °C. However, the mechanism should be further explored in near future.

$$C+H_2O=H_2+CO \qquad \Delta G^0 = 133100 - 141.63T \tag{5-9}$$

Direct reduction of molten FeO

The nut coke could also directly react with molten FeO when the temperature is above the melting temperature of iron ore (which is above 1400 °C as shown in this thesis) as Equation 5-10. It enhances the reduction degree and also increases the CO potential.

Carburization

Carburization takes place at the interface between nut coke and generated metallic iron shell when the nut coke makes contact with pellet in a local area in the case of interrupted experiment at 1100 °C. The carburization was identified by SEM-BSE-EDS image analysis as shown in Figure 5-17. Table 5-6 lists the chemical composition for the four tested points with EDS. EDS results indicate that the carbon content is around 2.5 wt%. It verifies that carburization takes place in the metallic iron shell when nut coke is close to pellet.



Figure 5-17 Macro image and micro-image of the pellet and metallic iron shell (Interrupted experiment at 1100 °C)

	C (wt%)	Fe (wt%)
Point 1	2.42	97.58
Point 2	2.32	97.68
Point 3	2.67	97.33
Point 4	2.59	97.41

Table 5-6 Chemical composition in metallic iron shell

The consumed nut coke protects the normal coke layer from reaction and reduces the direct reduction reaction caused by the normal coke layer. On the other hand, the consumed nut coke provides more CO and H_2 and increases the CO and H_2 potential through the Boudouard reaction and water-gas reaction.

5.4 Softening and melting behaviour

Softening and melting behaviour of the ferrous burden in the cohesive zone depends on each individual iron ore particle. A partly reduced iron ore particle consists of an oxide phase and a metallic iron shell. The properties of oxide phase and metallic iron shell have significant influence on the softening and melting behaviour of such an iron ore particle.

For the oxide phase, the chemical composition determines the melting temperature. Figure 5-18 is the CaO-SiO₂-FeO phase diagram [2]. It can be seen that the melting temperature decreases with the increase of the amount of FeO. It indicates that FeO promotes a low melting temperature. For the metallic iron shell, the softening temperature is governed by mechanical strength and the melting temperature is controlled by the carbon content in iron. A thick iron shell will produce a strong shell which can endure more pressure from the burden. Thus it has the ability to increase the softening temperature. Figure 5-19 shows that the melting temperature decreases with the increase of carbon content in iron [2]. This means that carburization will lower the melting temperature of the metallic iron.



Figure 5-18 CaO-SiO₂-FeO phase diagram [2]



Figure 5-19 Fe-C phase diagram [6]

5.4.1 Softening and melting temperature

As described in Chapter 4 the softening and melting behaviour could be derived from the displacement curve and pressure drop curve. The displacement curve shows the contraction and the expansion of the sample bed as a function of temperature or time. The pressure drop curve shows the differential pressure between the top and the bottom of the sample bed as a function of temperature or time.



Figure 5-20 Displacement curve during the reduction process

Figure 5-20 is a typical displacement curve for a pellet sample bed. 100 % displacement indicates the iron ore layer melts and drips completely. The case of 20 % nut coke could not reach to 100 % due to the remaining nut coke particles in the ore layer. The whole displacement curve could be divided into three stages. Stage 1 indicates the expansion and shrinking section, stage 2 demonstrates the softening section and stage 3 shows the melting section. The displacement curve starts with an almost flat line below 600 °C, followed by an expansion between 600 °C and 800 °C due to the phase transition (Fe₂O₃ \rightarrow Fe₃O₄). After that, it goes to the shrinking and softening sections due to the deformation of the pellet caused by increasing thermal and mechanical load applied on the sample bed. The last section is a rapid contraction from 1350 °C to 1500 °C caused by the carburisation

and melting process over a temperature range. The melting temperature is defined as the temperature at the maximum value of the pressure drop curve.

Figure 5-20 shows that the softening temperatures of 0 % nut coke case and 20 % nut coke case are 1014 °C and 1100 °C, respectively, and the melting temperatures of 0 % nut coke case and 20 % nut coke case are 1405 °C and 1420 °C, respectively. The softening and melting ranges (SM ranges) are 391 °C and 320 °C for 0 % nut coke and 20 % nut coke, respectively. The definition of SM range is the differential temperature between softening temperature and melting temperature. It is a very important index to represent the softening and melting properties. A small difference in temperature indicates a narrow SM range, i.e. a thin cohesive layer. A thinner cohesive layer leads a better softening and melting behaviour and it is beneficial for the permeability because the gas can go easily through the thinner cohesive layer.

Based on the description above, it can be found that the softening and melting behaviour is improved by mixing nut coke in the pellet layer. The softening and melting range decreases by 71 °C. Nut coke in the ore layer increases the reduction degree as found in Chapter 5.2. The increased reduction degree has two effects on the softening and melting behaviour. Firstly, a higher reduction degree causes a thicker metallic iron shell which can endure more pressure from the mechanical load. It will postpone the softening moment. On the other hand, the amount of FeO decreases due to the higher reduction degree in the final reduction stage. It is known that FeO could promote the low melting slag generation. Thus, a lower amount of FeO also makes a contribution to an increase of the softening temperature.

The pressure drop curve is also an important source to gain the information of softening and melting behaviour. For better understanding this behaviour, the pressure drop and displacement curves are combined in one figure (see Figure 5-21). The softening temperature is defined as the temperature whereby the pressure drop over the sample increases more than 5 %, compared to 20 measurements counted backwards. It is difficult to gain an accurate softening temperature by the pressure drop curve due to the tiny differential pressure at low temperature. The rough estimation of the softening temperatures are around 1000 °C and 1030 °C for the cases of 0 % nut coke and 20 % nut coke, respectively, based on this definition. The peak of the pressure drop curve shows a melting temperature. At that temperature the pressure drop will reach a maximum after which it will start to recover. The recovery is the result from melt dripping from the void and consequently the emptying of the void fraction thus lowering the pressure drop over the sample. The melting temperatures are 1425 °C and 1430 °C for the case of 0 % nut coke and 20 % nut coke, respectively. The melting temperature obtained from the pressure drop is slightly higher than the melting temperature derived from the displacement curve. To compare the two methods, a



direct observation approach was adopted to record the melting temperature and verify which method is closer to the real melting temperature.

Figure 5-21 The combination of displacement and pressure drop curves

Sinter and mixture of pellet and sinter were also tested to investigate the softening and melting properties by the interrupted experiments. The results are summarized in Table 5-7. The softening temperature of sinter is higher than that of pellets under RSM experimental conditions. The softening and melting temperature of the mixture is in between the pellet and sinter case. Both sinter and mixture testing demonstrate that the softening temperature increases by nut coke addition. The softening temperature increases by 36 °C and 38 °C for sinter and mixture, respectively. The melting temperature cannot be determined by interrupted experiments due to tests conducted below the melting temperature.

		Softening temperature
Pellet	0 % nut coke	1014 °C
	<u>20 % nut coke</u>	<u>1100 °C</u>
Sinter	0 % nut coke	1096 °C
	<u>20 % nut coke</u>	<u>1130 °C</u>
Misterra	0 % nut coke	1075 °C
wixture	20 % nut coke	1113 °C

Table 5-7 Softening temperature of different types of iron ore under the effect of nut coke interrupted at 1400°C

5.4.2 Melt dripping observation

As mentioned above, two approaches were used to determine the softening and meltdown temperatures. The results show that both methods could be used to obtain the softening and melting temperature. Although the melting temperatures obtained by the two methods are close to each other, it still has a difference of 10 °C~15 °C.

To gain more information about the melting temperature, two special viewports were designed for this purpose as shown in Figure 5-22. One of the viewports is assembled with a monitoring camera, which is used to capture the dripping molten iron and slag moments (the first dripping moment and complete dripping moment). The function of the other viewport is an inlet of LED light source for the monitor. The whole process of the dripping is recorded by the monitoring camera. The first dripping and complete dripping moments are obtained through video analysis.



Figure 5-22 Schematic view of the observation approach

Based on the captured dripping moment, the dripping temperatures collected in Table 5-8 were obtained.

 Table 5-8 First dripping and complete dripping temperature

	First dripping	Complete dripping	Dripping time range
	(°C)	(°C)	(min)
0 % nut coke	1410	1538	26
20 % nut coke	1407	1540	27

The camera observation shows that dripping is a process over a wide temperature range. The first dripping moment and the last dripping moment could be established by the camera monitor. It is hard to determine a so-called fixed melting temperature by this method. Unfortunately, there are no obvious differences found between the two cases, 0 % nut coke and 20 % nut coke.

Table 5-9 indicates that three approaches were used to determine the softening and melting properties. The first one is based on displacement curve, the second one is based on the pressure drop figure and the third one is based on direct observation by a camera monitor. The methods of displacement and the pressure drop demonstrate a similar trend that nut coke increases the softening temperature and that the melting temperature increases only very slightly.

Table 5-9 Obtained softening and melting properties from different methods

	Displac	ement	Pressu	ire drop	Obse	ervation
Mixing	Softening	Melting	Softening	Melting	First	Complete
ratio	_	-	-	-	dripping	dripping
0 %	1014 °C	1405 °C	1000 °C	1425 °C	1410 °C	1538 °C
20 %	1100 °C	1420 °C	1030 °C	1430 °C	1407 °C	1540 °C

5.4.3 Contraction of the sample bed

Figure 5-23, Figure 5-25 and Figure 5-26 present the contraction bed information for three series experiments. At 900 °C, the pellets and sinter begin to deform. It is just a tiny contraction right at the beginning. In a next step at 1100 °C, the iron ore continues to deform, but the shapes of pellet and sinter and also the void are still clear. When temperature goes up to 1300 °C, the deformation is becoming obvious and the pellets or sinter are closely connected to each other due to the load pressure. When temperature goes up to 1400 °C, the pellets or sinter are closely tight together, they even stick to each other and the voids disappear to a large extent. All the iron ore melt and drip at 1550 °C. The case of 1550 °C is a virtual column drawn by the displacement measurement. The case of 20 % nut coke could not reach 100 % contraction due to the remaining nut coke particles in the ore layer.



Figure 5-23 Bed contraction of pellet in the presence and absence (20%) of nut coke

Figure 5-24 is a combined figure for the displacement curve and the image analysis of the sample bed. Both ways illustrate the information of contraction degree. The image of the sample bed is obtained from the interrupted experiments at 900 °C, 1100 °C, 1300 °C and 1400 °C. The displacement curve is measured from the interrupted experiment at 1400 °C. The contraction degree determined by the two approaches demonstrates a similar trend but with a different value. Both ways indicate that nut coke reduces the contraction degree.

The images of sinter and the mixture of pellet and sinter were also obtained and they are shown in Figure 5-25 and Figure 2-26. They demonstrate a performance similar to the case of pellet.



Figure 5-24 Comparison of contraction degree obtained from image analysis and measured by displacement curve (interrupted at 1400 °C)



Figure 5-25 Bed contraction of sinter



Figure 5-26 Bed contraction of mixture

At 1400 °C, the pellets keep their partially spherical shape with a big cave in some pellets centres. However, the sinter particles have collapsed and stick to each other. The pores in the sinter bed are blocked if no nut coke is mixed with sinter. When mixing 20 % nut coke with sinter it shows a different behaviour. Figure 5-27 shows the sinter packed bed obtained from an interrupted experiment at 1400 °C. From Figure 5-27 it can be seen that nut coke acts as a skeleton in the packed bed and it postpones the moment that the voids disappear.



Figure 5-27 Nut coke acts as skeleton in sinter layer

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Table 5-10 is a summary of contraction degree for different iron ore types and Figure 5-28 is the stack column which is translated from Table 5-10. It indicates that the contraction degree of ferrous burden with 20 % nut coke is smaller than the cases of 0 % nut coke. It proves that nut coke has the ability to decrease the contraction degree and softening and melting properties for different types of iron ore.

lron oro	Casas	Temperature					
Iron ore	Cases	900 °C	1100 °C	1400 °C			
Pollot	0 % nut coke	0 %	15.8 %	57.8 %	63.1 %		
Fellet	20 % nut coke	0 %	14.2 %	33.3 %	47.8 %		
O instan	0 % nut coke	0 %	5.3 %	31.6 %	42.1 %		
Sinter	20 % nut coke	0 %	4.8 %	23.8 %	33.6 %		
Mixture	0 % nut coke	0 %	12.2 %	32.5 %	40.6 %		
	20 % nut coke	0 %	3.7 %	14.9 %	22.3 %		

Table 5-10	Summary	of contra	action degree
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Figure 5-28 Contraction degree of different types iron ore

A lower contraction degree accompanies a higher porosity which can be observed from Figure 5-27. They will directly lead to a lower pressure drop and a better permeability.

5.5 Permeability

The sample bed in the blast furnace may be defined as a kind of packed bed which is an assembly of various particles. The gas flow in the packed bed has an extremely significant influence on the performance of blast furnace.

Figure 5-29 is the pressure drop curve obtained from the full temperature range experiments. From Figure 5-29, it can be seen that the pressure drop almost keeps flat below 1000 °C and then goes up slightly below 1400 °C. It sharply reaches the maximum pressure drop around 1500 °C. There is no obvious difference below 1400 °C under this condition. The pressure drop curve of 20 % nut coke is lower than of 0 % nut coke when the temperature is higher than 1400 °C. The maximum pressure drop of mixing 20 % nut coke is 1398 Pa and the maximum pressure drop of mixing no nut coke is 1692 Pa. A lower pressure drop indicates a better permeability and it verifies that nut coke improves the permeability in the cohesive zone.



Figure 5-29 Pressure drop as a function of temperature (Full temperature range experiments)

All quenching cases have similar pressure drop performance, thus just one example is shown in Figure 5-30. It is hard to find any difference between the two cases below 1400 $^{\circ}$ C due to the sensor measurement range. The range is 0~6000 Pa for the differential pressure sensor used in the high temperature experiment. That is the reason why the measured data are not stable when the pressure drop is very small. The cold flow model experiment already proves that nut coke can improve the permeability in "dry zone". The sensor used in the cold flow model has a smaller measurement range 0~300 Pa (better sensitivity). It can measure the small pressure drop accurately.



Figure 5-30 Pressure drop below 1400 °C (Interrupted experiment at 1400 °C)

The explanation for this phenomenon is as follows: the direct reduction and carburization occur locally at the contacting area of pellet and nut coke. Therefore, the porosity grows with the melting of metallic iron at the boundary area. It forms a permeable matrix above 1400 °C that allows the melt to percolate through the bed and does not block the gas flow. Gas mainly passes through the coke matrix and the permeability of the packed bed is maintained sufficiently [1]. The nut coke in the cohesive layer can be also considered as a skeleton which is confirmed by Figure 5-27. Therefore channels for gas passage through this layer are formed.

This will contribute to improve the permeability. The second reason is verified that the permeability is improved by a narrower softening and melting range. Chapter 5.4 shows that the softening and melting range is narrowed by 71 °C through adding 20 % nut coke. A narrow softening and melting range means a thin cohesive zone. The gas passage through a thin cohesive layer is easier compared with a thick cohesive layer due to the high resistance in the thick cohesive zone.

The pressure drop in the cohesive layer is related to the contraction degree of the ore layer besides particle diameter and porosity in the Sugiyama formula [7] shown in Equation (5-11). It is used to calculate the pressure drop in the cohesive layer.

$$\frac{\Delta P}{L} = \left[\frac{1}{Cm}\right]^2 \left[\frac{1}{\Phi D_p (1-S_T)}\right] \left[\frac{\rho g u^2}{dD_p}\right]$$
Sugiyama formula (5-11)

Where

- ΔP Pressure drop, Pa
- L The distance, m
- *C* The discharge coefficient for orifice
- m Diameter ratio
- Φ The average shape factor
- D_p The average diameter of particles, m
- S_r The contraction of ore layers, %
- ρ_g The density of gas, kg/m³
- \tilde{g} The gravitational acceleration, m/s²
- *M* The mixed nut coke ratio
- ε The porosity of packed bed

Based on the Sugiyama formula, the pressure drop as a function of contraction degree is plotted in Figure 5-31. It indicates that the pressure drop goes up with increasing contraction degree. The pressure drop rises very quickly when the contraction degree is higher than 60 %. The contraction degrees obtained from Chapter 5.4 were used to calculate the relative pressure drop for the case of 0 % nut coke and the case of 20 % nut coke at different temperatures. Figure 5-31 demonstrates that there is no difference in pressure drop at 1100 °C. The pressure drop of 20 % nut coke is lower than 0 % nut coke by 8.9 % and 8.6 % for 1300 °C and 1400 °C, respectively based on the calculation. It proves again that nut coke can improve the permeability in the cohesive layer.



Figure 5-31 Calculated relative pressure drop based on the Sugiyama formula

5.6 Summary

Full temperature range experiments and interrupted experiments were conducted to investigate the reduction behaviour, softening and melting properties and permeability in the nut coke-ore layer. The experimental results give the following findings and observations.

The reduction degree of mixed charging (iron ore mixed with nut coke) is improved by using nut coke from a temperature of 800 °C upwards. The reaction rate keeps going up with increasing temperature up to 800 °C. Then the reaction rate goes down when the temperature is higher than 800 °C. The reaction rate of ore-nut coke mixed charging is higher than that of standard charging without nut coke participation. That the reaction rate goes down above 800 °C could be explained by the reduction retardation. With SEM-BSE-EDS image analysis, it further verifies that the reduction behaviour can be improved by nut coke-ore mixed charging. It shows a similar phenomenon with reduction curves calculated based on measured incoming-gas and off-gas profiles.

The loss of nut coke increases with temperature and almost 40 % nut coke are consumed in the reduction process. It proves that nut coke takes part actively in

the reaction and the confirmed reactions are: Boudouard reaction, water-gas reaction, direct reduction of molten FeO and carburization of metallic iron.

The softening temperature of adding no and 20 % nut coke are 1014 °C and 1100 °C, respectively, and the melting temperature of adding no and 20 % nut coke are 1405 °C and 1420 °C, respectively. The softening and melting range (SM range) are 391 °C and 320 °C for adding no and 20 % nut coke, respectively. Thus, the softening and melting range is narrowed by 71 °C.

The image analysis of the sample bed proves that nut coke has the ability to reduce the contraction degree and increase the reduction degree. It is confirmed that nut coke acts as a skeleton in the packed bed and it postpones the moment of void disappearance.

The pressure drop curve of adding 20 % nut coke is lower than that of 0 % nut coke when the temperature is higher than 1400 °C. The maximum pressure drop of adding 20 % nut coke is 1398 Pa and the maximum pressure drop of adding 0 % nut coke is 1692 Pa. It demonstrates that nut coke improves the permeability in the cohesive layer.
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6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

To investigate the effect and mechanism of nut coke on the performance of the blast furnace, cold flow model experiments and high temperature experiments with a newly developed RSM (Reduction Softening and Melting) set-up have been conducted for different nut coke mixing ratios. Nut coke mixing ratio means the weight percentage nut coke of total coke rate (300 kg/tHM).

Cold flow model experiments reveal that adding nut coke into an ore layer of the blast furnace will improve the permeability in the dry zone.

- The size of nut coke (10~15 mm, 15~20 mm, 20~25 mm and 25~30 mm) have little difference on the pressure drop. Measured and calculated porosity results indicate that the porosity increases with the increase of nut coke mixing ratio for each size nut coke except for the 25~30 mm nut coke.
- The optimum nut coke mixing ratio for the four kinds of nut coke is 20 %~30 %.
- Pellet, sinter and a mixture of pellet and sinter have similar permeability performance under the effect of nut coke.
- Multi-layers testing shows that less charging layers are beneficial to obtain a better permeability.
- CT image analysis demonstrates that the porosity of the interface is around 0.3 (30 %) due to iron ore filling in the gaps among the big sized coke particles. It is lower than the porosity of the individual ore layer and coke layer. CT image analysis also confirms that the porosity of 30 % nut coke is higher than 20 % and 10 % nut coke.
- The model results show good similarity with the experimental results. The optimum mixing ratio is 30 % for a two layers "unit cell" structure.

The results of high temperature experiments show that adding nut coke increases the reduction degree and improves softening and melting and enhances the permeability.

- The reduction degree of mixed charging (iron ore mixed with nut coke) is improved by nut coke from temperatures at 800 °C and upward. The Boudouard reaction and water-gas reaction, promoted by the nut coke, are two of the key reasons for enhancing the reduction degree. It is proven by the off-gas analysis and SEM-BSE-EDS.
- Carbon mass balance calculation shows that the loss of nut coke increases with temperature and almost 40 % of the nut coke is consumed in the reduction process under the simulated blast furnace conditions. It further

proves that nut coke takes part actively in the reaction. Nut coke contributes to reduce the starting temperature of the Boudouard reaction and water-gas reaction.

- The softening temperature increases by 86 °C and the softening and melting range decreases by 71 °C when adding 20 % nut coke in the ore layer.
- The displacement curves and the image analysis of the sample bed prove that nut coke has the ability to decrease the contraction degree of the sample bed.
- The maximum pressure drop of adding 20 % nut coke is 1398 Pa and the maximum pressure drop of no nut coke in the ore layer is 1692 Pa. Quenching experiments confirmed that the nut coke in the cohesive layer acts as a skeleton and maintains a high porosity which contributes to the improvement of the permeability. The reduced contraction degree by nut coke also contributes to the enhancement of the permeability.

6.2 Recommendations

- In order to make a more accurate determination of weight loss and reduction degree, the RSM set-up should be improved with loading cells under the furnace support. The existent electronic balance does not function adequately due to the friction between the bottom flange and the support tube and also the friction between the crucible and the reaction tube. To avoid the influence of friction, high definition loading cells should be installed on the bottom of the whole set-up. Then the developed RSM has the function of recording the sample weight changes during the experiment.
- A wide range of nut coke size and nut coke mixing ratios should be tested for the full range of heating profiles up to 1550 °C. Due to restrictions arising from the manufacture of the furnace body, only one nut coke size (10~15 mm) and one nut coke mixing ratio (20 %) could be tested for the full range of temperature profile in this study. Different sizes and different mixing ratios may lead to a different performance on reduction kinetics and softening and melting behaviour in the high temperature region.
- Some isothermal experiments should be conducted to obtain the key parameters for better understanding the reduction mechanism and a kinetics model could be constructed based on the conditions of mixing nut coke in the ore layer.

SUMMARY

The blast furnace consumes a large amount of high quality metallurgy coke (size 35-80 mm) in addition to ore in the form of pellets and sinter. This coke is the coarse fraction, derived from the coke plant. The fine fraction (8 -35 mm), arise after sieving, named nut coke, can't be directly used in blast furnace. The fraction of smaller than 8 mm is used in the sinter plant. Therefore, a large fraction of coke around 20 % from coking plant/process is not used for iron ore reduction. Recent research indicates that usage of nut coke will be economic if properly used. Nut coke cannot be directly mixed with normal coke because it will decrease the permeability of the coke layer in the blast furnace. However, mixing nut coke into the ferrous burden layer could be an effective way to use the coke resource economically. This mixed charging could improve softening and melting behaviour, reduction kinetics and permeability and also make full use of the coke resource. It may, however, also worsen the layer permeability and even deteriorate the whole blast furnace process. The mechanism of the effect of mixing nut coke into the ferrous burden on the performance of the blast furnace is still not clear, and thus the usage of nut coke is still limited.

To investigate the effect and mechanism of using nut coke in the ferrous burden on the performance of the blast furnace, cold flow model experiments and high temperature experiments have been conducted. An advanced Reduction, Softening and Melting experimental facility (RSM) was designed for high temperature experiments at TU Delft.

In support of process scale-up, the use of cold flow modelling is a core competency in the process metallurgy field. Typically, the model is designed and fabricated of steel and/or plastic in a size that is large enough to minimize mass transfer and wall effects. Using these models, qualitative and quantitative measurements can be made to help verify and optimize operating parameters for a variety of gas-liquid and/or gas-solid systems. These measurements include mixing, separation, pressure drop, porosity and/or density. The results of the cold flow model for this thesis are just valid in the blast furnace "dry zone". Compared with high temperature experiments, it is a low cost, short test period experimental technology. The other extremely important issue is that it is easy to test full size coke. Normally, the crucible diameter of a high temperature experimental set-up in the laboratory is limited by high temperature technology and investment budget. For the cold model, it is very convenient to build a big size reactor by plexiglass with a low investment. However, it is difficult or impossible to simulate high temperature behaviour of iron ore reduction and can never replaces the function of a high temperature experimental system.

Chapter 6 Conclusions and recommendations

Industrial pellet, sinter and coke are used in the cold flow model study. The pellet size is 10~13 mm, sinter size is 10~15 mm, and nut coke sizes are divided into 4 groups: 10~15 mm, 15~20 mm, 20~25 mm and 25~30 mm. The size of normal coke in a coke layer is 40~50 mm. Four kinds of charging patterns and five kinds of nut coke mixing ratios were tested. The nut coke mixing ratio is the weight percentage of nut coke as part of the total coke in the blast furnace. For example, a coke mixing ratio of 20 % means that 60 kg nut coke is mixed with ore and 240 kg coke is in the coke layer under a constant coke rate of 300 kg/tHM.

The cold flow model experiments confirm that adding nut coke into an ore layer of the blast furnace will improve the permeability in the dry zone. The size of nut coke (10~15 mm, 15~20 mm, 20~25 mm and 25~30 mm) makes little difference on the effect of pressure drop. The optimum nut coke mixing ratio for the four kinds of nut coke is 20 %~30 %.

High temperature experimental studies aim to increase the knowledge of the complex process of reduction, softening and melting and permeability in the blast furnace under the condition of mixing nut coke into an ore layer. The laboratory studies include the investigation of the influence of nut coke mixing ratio and nut coke size under different reducing conditions. To describe the processes of reduction and melting of burden materials, a large number of experiments is interrupted at different stages of the reduction. Obtained materials are studied by XRD, XRF and SEM-BSE-EDS.

During the RSM testing, temperature and gas profiles can be altered with time to simulate specific blast furnace conditions. The off-gas pipe is connected to a gas analyser which is used to analyse the composition of the mixing gas. The pressure drop, over the packed bed, is measured by a differential pressure sensor. The contraction of the sample bed is measured by a displacement sensor. There is a sample collector on the bottom of the furnace for collecting the molten iron and slag samples. The sample dripping status can be observed and recorded by a video camera through a glass viewport.

Compared with the cold flow model experiment, it runs under a simulated blast furnace gas and temperature profile with iron ore and coke used in an industrial blast furnace. Thus, the high temperature experiment has the ability to investigate the complicated chemical reactions and physical changes of iron ore in the cohesive zone. It is direct information for industrial blast furnace operation. The cold flow model experiment demonstrates that the nut coke mixing ratio of 20 ~30 % is the optimum parameter to obtain the best permeability. Thus, a nut coke mixing ratio of 20 % was tested in high temperature experiments with the RSM set-up to further study the effect and mechanism of nut coke on reduction kinetics, softening and melting behaviour and permeability in the cohesive layer.

Chapter 6 Conclusions and recommendations

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The experimental results indicate that adding nut coke increases the reduction degree and improves softening and melting and enhances the burden permeability. The mechanism of nut coke consumption in the ore layer is analysed. The fundamentals why adding nut coke improves the reduction, softening and melting properties and permeability of the blast furnace are also investigated in this thesis. The cold flow model experiments and high temperature experiments prove that adding nut coke into an ore layer will improve the blast furnace performance. Finally it decreases the cost of producing of a tonne of hot metal and eventually reduce the environment impact by saving normal coke.

SAMENVATTING

De hoogoven gebruikt naast erts in de vorm van sinter en pellets een grote hoeveelheid hoogwaardige metallurgische kooks (grootte 35 - 80 mm). Deze kooks is de grove fractie, afkomstig van de kooksfabriek, de fijne fractie (8 -35 mm), ontstaan na het afzeven, noemt met kleintje kooks (eng; nute coke). De fractie kleiner dan 8 mm wordt gebruikt in de sinterfabriek. Een groot deel van de kooks, ongeveer 20%, uit de kooksfabriek, wordt dus niet direct gebruikt voor de reductie van ijzererts. Recent onderzoek toont aan dat het gebruik van kleintje kooks economisch gunstig kan zijn indien dit op de juiste manier wordt toegepast. Kleintje kooks wordt van de grove kooks gescheiden omdat het de permeabiliteit van de kookslaag in de hoogoven verlaagt. Het mengen van kleintje kooks in de ijzerhoudende laag in de hoogoven is echter een effectieve manier zijn om de beschikbare kooks economisch te gebruiken. Dit gemengd beladen kan het verweken en smelten van de ertslaag verbeteren. Het is bovendien gunstig voor de reactiekinetiek en permeabiliteit van de ertslaag, en daarnaast zorgt het ook voor een volledig gebruik van de geproduceerde reductiemiddelen. Kleintje kooks kan echter ook de doorlaatbaarheid van de laag verslechteren en zelfs het volledige hoogovenproces negatief beïnvloeden. Het mechanisme van het effect van menging van kleinje kooks in de ijzerhoudende laag op de prestaties van de hoogoven is nog niet helemaal duidelijk en daarom is het gebruik van kleintje kooks beperkt.

Om het effect en het mechanisme van het gebruik van kleinje kooks in de ijzerhoudende laag op de prestaties van de hoogoven te onderzoeken, zijn koude stromingsmodel experimenten en experimenten bij hoge temperaturen uitgevoerd. Een geavanceerde proefopstelling voor reductie-, verweking-, en smelt experimenten (RSM) bij hoge temperaturen is ontworpen aan de TU Delft.

Ter ondersteuning van het opschalingsproces, is het toepassen van koude stromingsmodellen een kernactiviteit bij het proces metallurgie onderzoek. Gewoonlijk wordt het model ontworpen en vervaardigd uit staal en/of kunststof in een formaat dat groot genoeg is om massaoverdracht en wandeffecten te minimaliseren. Met deze modellen kunnen kwalitatieve- en kwantitatieve metingen worden uitgevoerd om bedrijfsparameters voor allerlei gas-vloeistof en/of gas-vast systemen te verifiëren en te optimaliseren. Deze metingen omvatten mengen, scheiden, drukval, porositeit en/of dichtheid. De resultaten van het koude stromingsmodel voor dit proefschrift zijn slechts geldig in de schachtzone of droge zone van de hoogoven (hier wordt de lading vanaf bunkertemperatuur op een temperatuur van ca. 1100 °C gebracht, de verweek temperatuur van de ertsen). In vergelijking met de hoge temperatuur experimenten is het een goedkope experimentele technologie met een korte testperiode. Een ander zeer belangrijk

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punt is het feit dat het gemakkelijk is om kooks van normale grootte te testen. Doorgaans wordt de diameter van de smeltkroes in een proefopstelling voor pyrometallurgische experimenten in het laboratorium beperkt door de hoge temperatuur technologie en het investeringsbudget. Voor het koude stroom model, is het erg handig om een groot formaat reactor van plexiglas te bouwen met een lage investering. Het is echter moeilijk of zelfs onmogelijk om het hoge temperatuurgedrag van ijzererts reductie hiermee te simuleren en kan dus de werking van een experimenteel hoge temperatuur systeem niet vervangen.

In het koude stromingsmodel onderzoek worden industriële pellets, sinter en kooks gebruikt. De korrelgrootte van pellets is 10~13 mm, de sintergrootte is 10~15 mm en de kleinje kooks maten zijn verdeeld in 4 groepen: 10~15 mm, 15~20 mm, 20~25 mm en 25~30 mm. De grootte van normale kooks in een kookslaag is 40~50 mm. Vier manieren van beladen en vijf verschillende kleinje kooks mengverhoudingen zijn getest. De kleinje kooks mengverhouding is het gewichtspercentage ervan als onderdeel van de totale hoeveelheid kooks in de hoogoven. Bijvoorbeeld, een kooks mengverhouding van 20% betekent dat 60 kg kleinje kooks is gemengd met erts en 240 kg kooks aanwezig is in de kookslaag onder een constante toevoer van 300 kg kooks per ton ruwijzer.

De koude stromingsmodel experimenten bevestigen dat het toevoegen van kleinje kooks in een erts laag van de hoogoven de permeabiliteit in de droge zone zal verbeteren. De grootte van de kleinje kooks (10~15 mm, 15~20 mm, 20~25 mm en 25~30 mm) maakt weinig verschil op het effect van drukval. De optimale kleinje kooks mengverhouding voor de vier soorten kleinje kooks is 20%~30%.

Experimenteel hoge temperatuur onderzoek heeft tot doel de kennis van het complexe proces van reductie, verweking en smelten en permeabiliteit in de hoogoven te verhogen onder de condities van menging van kleinje kooks in een erts laag. De laboratoriumproeven omvatten het onderzoek naar de invloed van de kleinje kooks mengverhouding en de grootte van kleinje kooks onder verschillende reducerende omstandigheden. Om het proces van reductie en smelten van de lading in de hoogoven te beschrijven zijn een groot aantal experimenten afgebroken in verschillende stadia van het reductieproces. De verkregen materialen zijn geanalyseerd en onderzocht met XRD, XRF en SEM-BSE-EDS.

Tijdens de RSM testen kunnen temperatuur, en gas samenstellingsprofielen worden veranderd als functie van de tijd om de specifieke hoogoven condities te simuleren. De uitlaatgasleiding wordt aangesloten op een gasanalysator die wordt gebruikt om de samenstelling van het menggas te meten. De drukval in het gepakte bed wordt gemeten met een differentiële druksensor. De inkrimping van het monster bed wordt gemeten door een verplaatsingssensor. Er is een monster collector op de bodem van de oven voor het verzamelen van gesmolten ijzer en

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slak monsters. De toestand van het gesmolten druipende materiaal tijdens de reductie kan worden waargenomen en vastgelegd door een videocamera via een glazen kijkvenster.

De resultaten van de hoge temperatuur experimenten zijn geldig in de zogenaamde smelt en verwekingszone (cohesieve zone) gevolgd door de druppelzone van de hoogoven. In vergelijking met het koude stromingsmodel experiment, wordt het experiment uitgevoerd onder een gesimuleerd hoogovengas- en temperatuurprofiel met ijzererts en kooks zoals in een industriële hoogoven wordt gebruikt. Derhalve biedt het hoge temperatuur experiment de mogelijkheid om de ingewikkelde chemische reacties en fysische veranderingen van ijzererts in de cohesieve zone te onderzoeken. Het verschaft directe informatie over de werking van de hoogoven op industriële schaal. Het koude stromingsmodel experiment toont aan dat de kleinje kooks mengverhouding van 20~30% de optimale parameter is om de beste permeabiliteit te verkrijgen. Aldus werd een kleinje kooks mengverhouding van 20% getest in hoge temperatuur experimenten met de RSM opstelling tot verdere bestudering van de werking en het mechanisme van kleinje kooks reductor op de reactiekinetiek, het verwekingsproces, het smelt-gedrag en de permeabiliteit in de cohesieve laag.

De experimentele resultaten tonen aan dat door het toevoegen van kleinje kooks de reductiegraad toeneemt, de verweking en smeltgedrag verbetert en de permeabiliteit van de erts laag in de oven verhoogd wordt. Het mechanisme van het verbruik aan kleinje kooks in het erts laag is bestudeerd. Waarom het toevoegen van kleinje kooks de reductie-, verweking-, en smelteigenschappen verbetert en de permeabiliteit van de hoogoven verhoogt, is ook fundamenteel onderzocht in dit proefschrift.

De koude flowmodel experimenten en hoge temperatuur experimenten bewijzen dat het toevoegen van kleinje kooks aan een erts laag de hoogoven prestaties zal verbeteren. Tenslotte zal het de kosten voor de industriële productie van een ton ruwijzer verlagen en uiteindelijk de milieubelasting verminderen door een lager gebruik van normale kooks.

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