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Study on the Process of Preparing Nickel-Iron Alloy by Hydrogen Selective Reduction

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Abstract. Recycling of nickel metal from nickel-containing spent catalysts can not only alleviate the contradiction between supply and demand, but also guarantee the demand of national strategic reserve metal, which is of great strategic significance. With reference to the gas-based shaft furnace-electric furnace short flow process in iron and steel metallurgy, this study proposes to treat nickel-containing waste catalysts with hydrogen as a reducing agent and to prepare nickel-iron alloys by using high-temperature melting process. The mechanism of selective reduction of Ni in waste catalysts by hydrogen was investigated by simulation analysis, NiO will react rapidly with hydrogen at lower temperatures to produce Ni, and the reduction of Fe_2O_3 is greatly affected by the temperature and the reaction is a cascade reaction of Fe_2O_3, Fe_3O_4, FeO, Fe. Under the conditions of hydrogen concentration of 60vol.%, reduction temperature of 800 ℃, reduction time of 90 min, and pellet diameter size of 10 mm, the metallization rates of Ni and Fe reached 92% and 50%, respectively.Under the conditions of melting temperature of 1500 ℃, melting time of 4 h, iron trapping agent addition of 12% of the mass of raw materials, and carbon reducing agent addition of 4% of the mass of raw materials, the recovery rate of nickel in the spent catalyst reached 99%. Recycling requirements have been met. This study provides an efficient recovery method for the enrichment of metallic nickel by high-temperature smelting.

Keywords: Hydrogen reduction; Nickel-containing spent catalysts; Resource recycling.

1. Introduction

Nickel (Ni) is a silver-white metal, itself has a certain degree of hardness and ductility, is an important strategic metal, widely used in stainless steel, new energy and other fields.The rational utilization of nickel resources is of great significance in promoting the sustainable development of China's chemical industry, new energy industry, and aerospace manufacturing industry[1-2]. The content of nickel in waste failed nickel-containing catalysts ranges from about 1.2% to 6% at low levels to 60% to 90% at high levels, whereas silicon-nickel ores used for smelting metals contain only 2.8% nickel, so effective recovery of Ni from nickel-containing waste catalysts can yield great environmental and economic benefits[3-4].

Traditional Ni recovery processes are mainly focused on hydrometallurgical processes. The nickel-containing spent catalyst is ground and treated with an acid solution to dissolve the Ni into the solution and separate it from the carrier.However, the wet recovery process still has the following problems: long recovery process, high material consumption, large amount of subsequent leaching wastewater, and challenging direct leaching and extraction of Ni from nickel-containing spent catalysts[5-6]. Yi-Chieh Lai et al.[7] studied the recovery of valuable metals from spent hydrodesulfurization (HDS) catalysts by mixed acid leaching and fluidized bed electrolysis processes. In addition to wet leaching recovery, pyrometallurgy is also an important method for Ni enrichment. In the fire enrichment process, the trap metal forms an alloy with Ni and the carrier slagging to achieve Ni enrichment[8].Wang Chengyan et al.[9] used waste hydrogenation catalysts from petrochemical industry as raw materials, which were mixed with certain content of lignite reducing agent, trapping agent, slagging agent and co-solvent for trapping and melting in melting furnace to realize slag-gold separation in the furnace.Antola O et al.[10] carried out experimental

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studies on roasting reduction of nickel ferro sulphide and nickel-bearing nickel laterite ores in a horizontal tube furnace and a laboratory scale fluidized bed reactor.

Hydro-metallurgical process is an increasingly emerging metallurgical process in iron and steel metallurgy nowadays. Against the background of the scarcity of coal resources in China, there is an urgent need to apply new renewable and clean energy sources to the metallurgical industry.The process before the main use of hydrogen and carbon monoxide gas mixture as a reductant, the ideal process state is to make the iron and steel metallurgical industry to get rid of the dependence on fossil energy, the use of hydrogen will be in the mineral metal oxides directly reduced to metal monomers, the reduced material into the resistance furnace melting to form an alloy, the production efficiency is greatly improved[11-13].

The efficiency of Ni recovery using hydrogen reduction of nickel-containing waste catalysts directly under high temperature conditions is low, and it is difficult to realize the separation of nickel-iron alloys. Therefore, it is necessary to utilize high-temperature melting to enrich nickel-iron alloys. In this study, the spent catalyst was first mixed with auxiliary materials for pelletizing, and hydrogen reduction of nickel-containing spent catalyst oxidized pellet experiments were carried out. After selective reduction of nickel-containing waste catalyst with hydrogen, the reduced product is ground and mixed with appropriate flux, and finally the mixture is put into a resistance furnace for high-temperature melting to realize the separation of the slag phase from the alloy phase and obtain the nickel-iron alloy with high Ni content.

2. Simulation Section

2.1 Modeling and Solution Setup

Simulation study for the reduction section of the shaft furnace hydrogen reaction process research, due to the whole three-dimensional model of the shaft furnace furnace structure is more complex, the need to simplify the reaction process and approximate calculations, and then does not affect the content of the study on the basis of the reduction section of the shaft furnace is simplified to a height of 6 m, the radius of the rotating axisymmetric structure of the two-dimensional axis symmetrical model of the 3 m, the reduction of the gas into the entrance from the lower part of the entrance to the bottom of the shaft furnace upward movement, and downward movement of materials, fully in contact, the reduction reaction, the reduction of Fe_2O_3 and NiO in the spent catalyst material into Fe and Ni. The reduction gas enters from the bottom of the shaft furnace, moves upward, and fully contacts with the materials moving downward to carry out the reduction reaction, which reduces Fe_2O_3 and NiO in the spent catalyst materials to Fe and Ni. After the reaction is completed, the reduction gas is discharged from the reduction gas outlet located at the top of the furnace. The established two-dimensional model of the reduction section of the shaft furnace is meshed, the grid cell size is 5 mm, and the boundary is named, and the two-dimensional shaft furnace grid model is shown in Fig. 1.

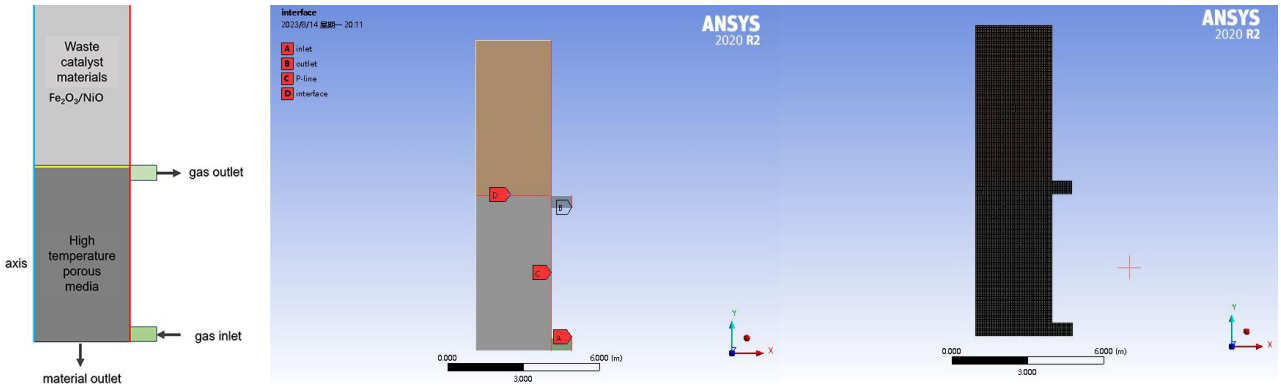

Fig. 1 2D Shaft Furnace Mesh Model

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The hydrodynamic equations are the basis for solving chemical reactions, including mass conservation equation, energy conservation equation, momentum conservation equation and mass diffusion equation, etc[14-15], and the corresponding parameters are set to theoretically analyze and numerically simulate the chemical reaction process in the reduction section of the shaft furnace. The reducing gas inlet is set as velocity inlet, the starting temperature of porous media solid material is 300 K, the blowing volume is set as 2500 Nm^3/t, the gas velocity is set as 10 m/s, the inlet reducing gas temperature is set as constant value 1093 K, the slip grid is used in the calculation to simulate the real movement of the charge, and the slip velocity is $2.5x10^{-4}$ m/s. The outlet is set as pressure outlet, the pressure is set at 40 kPa, and the temperature of the reducing gas outlet is set at 723 K. The porous medium model is used for simulation, the viscous drag coefficient is taken as 1.58e8 m^{-2}, the inertial drag coefficient is taken as 16963 m^{-1} and the wall heat loss is neglected.

2.2 Composition Distribution of Reduction Process

When the reduction temperature is 800 ℃, the diameter of the material pellet is 12 mm, and the hydrogen concentration is 100%, the changes of different oxides in the shaft furnace with the height of the shaft furnace are shown in Fig. 2. As can be seen from the figure, with the decline of the material pellet of nickel-containing waste catalyst, NiO can rapidly undergo reduction reaction with hydrogen to form Ni, and part of the Fe_2O_3 reaction can be seen in Fig. 2 b, c, d, when the material descends by 0.4 m, all of the Fe_2O_3 reacts to become Fe_3O_4, and it reacts to become FeO by about 0.7 m. And it can be seen in Fig. 2 e, when the material descends by a height of 2.8 m, the material is basically completely reacted, and the metallization rate of the final material is about 95%, which indicates that NiO reacts rapidly, while the reaction of Fe_2O_3 is carried out step by step from $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.

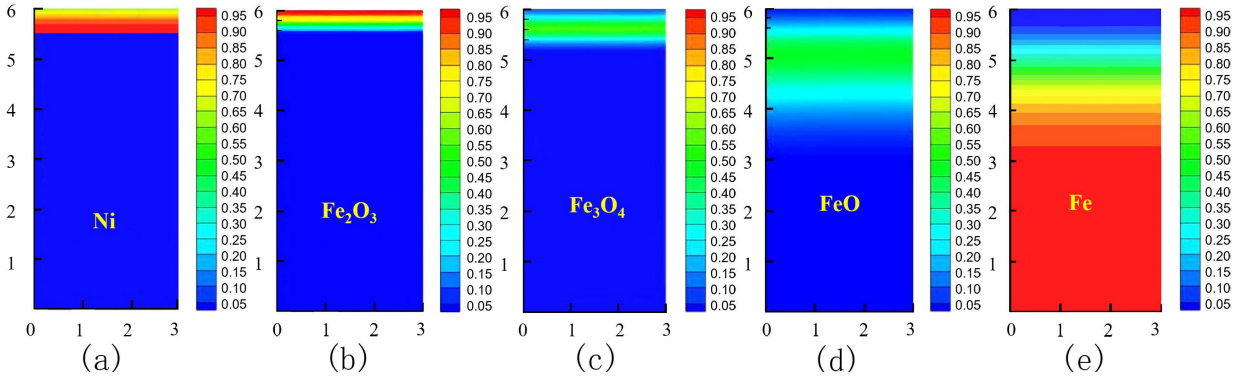

Fig. 2 Variation of different oxides in the shaft furnace with height of the shaft furnace

3. Experimental Part

3.1 Experimental Study of Hydrogen Selective Reduction

3.1.1 Preparation process of pellets

Material pellets are made in a 300 mm diameter disc pelletizing machine, set the rotational speed of 30 rpm, the linear speed is 1 m/s. Firstly, take the nickel content of 11.5% waste catalyst, grinding to 120 mesh, drying and Fe_2O_3 fine powder according to the mass ratio of 1:4 for mixing, after mixing the material with the quality of 5% of the bentonite clay, artificial mixing, adding water, and mixing and so on, the mixture of materials, moisture control 6% ~ 7%, take a small amount of material into the ball tray, uniformly add water to create a master ball, the waste catalyst by rolling molding, the nickel-containing waste catalyst wetted with water and Fe_2O_3 powder in the rolling process by the mechanical force and capillary action to become a sphere, fine particles rely on the force of the capillary action between the capillary force, molecular gravity, friction and so on to make the ball with a certain degree of strength. Finally, the spheres with diameters ranging from 0.4 cm to 1.6 cm were prepared. The temperature of the muffle furnace was raised to 600 ℃, and

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then the pellets after drying in the blast drying oven were put into the muffle furnace, the door of the furnace was closed, and air was blown into the furnace to ensure the oxidizing atmosphere inside the furnace, and then it entered into the preheating stage, and the temperature of the furnace was slowly raised to 1000 ℃, and the pellets were roasted at a constant temperature of 1000 ℃ for 30 min, and the pellets were roasted for 30 min. After the pellets were roasted, the power was turned off, and we waited for the temperature of the furnace to be naturally cooled down to the room temperature, and then we took out the finished nickel-containing waste catalyst Oxidized pellets.

3.1.2 Experimental setup and experimental procedure

The setup for the experiment of selective reduction of nickel-containing spent catalyst pellets with hydrogen consists of a PEM electrolyzer for hydrogen production by electrolyzing water and a shaft furnace reaction unit. with a quartz tube as the reaction vessel, with a specification of 45×600 mm and a thickness of 3 mm, and a stainless steel shell made of asbestos and pickaxe cotton, a thermocouple is placed inside the furnace to measure the temperature, and three silicon carbon rods are used to warm up and heat the quartz tube reactor, and a temperature control box precisely controls the temperature change. A temperature control box was used to control the temperature precisely. The quartz tube had an opening at the top and a 10 mm diameter round port near the bottom 80 mm, which was connected to the inlet of the reducing gas. Hydrogen was used as the reducing gas and nitrogen was used as the protective gas. The gas flow rate and gas volume fraction were controlled by a valve and a mass flow meter, and the spent catalyst pellet was placed in the middle of the quartz tube shaft furnace in the constant temperature area.

At the beginning of the experiment, the spent catalyst pellet was firstly placed in the middle of the vertical furnace, and nitrogen was used as the protective gas to fill the tube, and then the temperature was increased, and when the expected temperature was reached, the valve was controlled to pass in the reducing gas to carry out the reduction experiment. Under this experimental setup, the effects of reduction temperature, hydrogen concentration, reduction time, and size of spent catalyst pellet on the metallization rate of Ni and Fe were investigated.

3.1.3 Reduction experiment results and analysis

The effect of Ni and Fe metallization rate with the change of each factor is shown in Fig. 3, which shows that when the reduction temperature is increased from 600 ℃ to 800 ℃, the Ni and Fe metallization rate shows an increasing trend, and when the temperature is continued to be increased to 1000 ℃, reduction of iron oxides gives rise to the low melting point eutectic 2FeO-SiO, which inhibits FeO from further being reduced to metal Fe, so that the iron metallization rate shows a decreasing trend; When the reduction time is short, the rate of reduction of FeO to Fe by H_2 is lower than the rate of reduction of Fe_2O_3 to FeO, and the rate of metallization is lower, with the increase of time, H_2 goes to the inside of the pellet by internal diffusion, which leads to the reduction of more Ni and Fe oxides to metallic Ni and Fe, and the metallization rate gradually increases, therefore, the longer the reduction time, the more conducive to the increase of Ni, Fe metallization rate, when the reduction time of more than 90 min, Ni, Fe metallization rate are tending to equilibrium; Hydrogen concentration of Ni, Fe metallization rate is not significant, hydrogen concentration at 20vol.% is excessive relative to the conditions of this experiment, and after the hydrogen content of the gas mixture is optimized, increasing the hydrogen concentration has less effect on the Ni and Fe metallization rates; Pellet diameter of 4 mm ~ 10 mm, Ni, Fe metallization rate increased, but continue to increase the pellet diameter, the rate of metallization is reduced, the experimental under this experimental condition, the size of pellet diameter is more suitable at about 10 mm. Under the conditions of hydrogen concentration of 60vol.%, reduction temperature of 800 ℃, reduction time of 90 min, and pellet diameter size of 10 mm, the metallization rates of Ni and Fe reached 92% and 50% respectively. From the experimental results, it can be seen that the hydrogen reduction during the experiment has basically the same trend as the direction of the simulation results.

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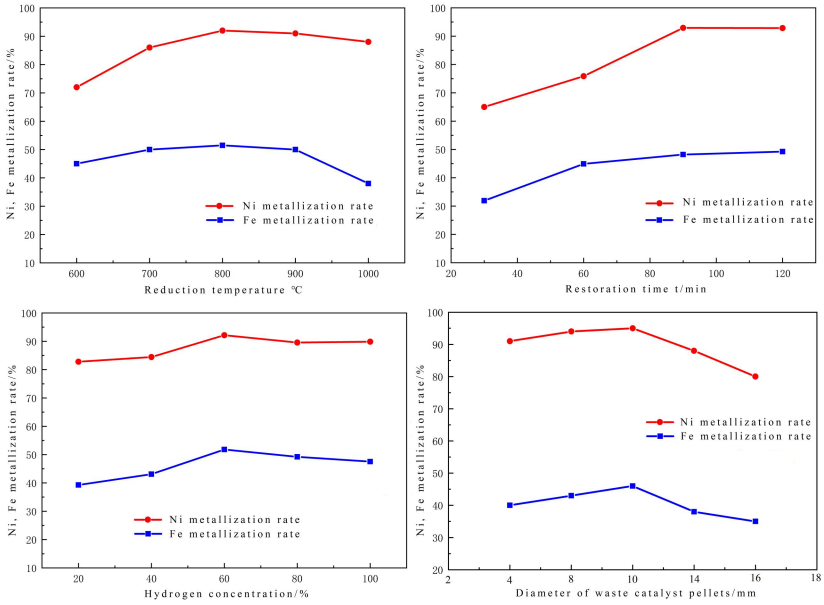

Fig. 3 Effect of variation of Ni and Fe metallization rates with various factors

3.2 Experimental Study of Melting Nickel-Iron Alloy at High Temperature

3.2.1 Preparation of melting materials

The raw material for melting is the spent catalyst pellet after selective reduction by hydrogen. Melting, need to add a small amount of coke powder, the role of coke can make the material in the unreduced iron oxides and a very small amount of nickel oxides reduced to metallic iron and metallic nickel, after the reduction of metallic iron can be added with the iron powder together to play the role of the trapping agent, the other auxiliary materials, including slagging agent and iron trapping agent.

3.2.2 High-temperature melting experimental equipment and methods

This melting alloy experimental equipment is mainly a high temperature resistance furnace, melting container for the graphite crucible,specifications for the inner diameter of 50 mm, a height of 120 mm, thickness of 5 mm, the upper layer of melting slag with another graphite crucible to take out the specifications for the inner diameter of 30 mm, a height of 100 mm, a thickness of 5 mm. The high-temperature resistance furnace for melting alloys is heated by silicon molybdenum rods.After the reduction of the waste catalyst pellets crushed, ground to 120 mesh, with the trapping agent Fe fine powder, slagging agent and a small amount of carbon reductant in accordance with a certain proportion of fully mixed, uniformly mixed in the graphite crucible, and then put into the resistance furnace, open the temperature control box, the heating furnace for the temperature program settings, manually warming up to 300 ℃, switched to automatic warming, warming up to 1500 ℃, a constant temperature of 3 h high temperature melting, after the temperature in the furnace through the program cooling and natural cooling to room temperature, take out the graphite crucible, weigh it, separate the alloy phase from the slag phase, take the slag phase detection, calculate the recovery rate of nickel metal, detect the physical combination of nickel-iron alloys, and get the finished product of nickel-iron alloys.

3.2.3 Melting experiment results and analysis

Nickel metal recovery with the smelting process of the various factors of the changes shown in Fig.4 , Fig.4 shows that the addition of trapping agent from 4% to 8%, the results of the smelting experiment has a greater impact on the recovery of nickel metal from 57% to 94%, continue to increase the amount of trapping agent, nickel metal recovery in the addition of trapping agent for the mass of raw materials 12% to reach the maximum value of 98.6%, after reaching the maximum

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value increase, nickel metal recovery did not change much. In the process of melting alloy at high temperature, the slag floats up, it can not be avoided that there will be a small amount of nickel metal is brought into the slag, the iron trapping agent can not be done to trap all the nickel metal to. Adequate addition of trapping agent, can make the melting process of iron metal and nickel metal more fully in contact, but the amount of trapping agent added to a certain extent, there will still be a small portion of the nickel metal is brought into the slag phase, so as to increase the amount of trapping agent added, the nickel metal recovery is no longer a significant change. When the amount of carbon reducing agent is increased from 1% to 4% of the mass of raw material, the recovery of nickel metal increases from 60% to the maximum value of 98.2%, and the recovery of nickel metal decreases slightly when the amount of reducing agent continues to increase. When the carbon reductant is added in the right amount, it is just enough to reduce the unreduced iron oxides in the spent catalyst to iron, and the other small amount of metal oxides will be reduced to metal monomers into alloys. During the process of temperature from 1350 ℃ to 1400 ℃, the recovery of nickel in the spent catalyst increased from about 41% to about 80%, and continued to increase the melting temperature to 1500 ℃, the recovery of nickel metal reached more than 98%, and the temperature continued to increase, the recovery of nickel was less changed to a certain extent, and when the melting temperature was more than 1550 ℃, the nickel recovery showed a decreasing trend. With the increase of melting time from 2 h to 3 h, the recovery of nickel in the nickel-containing waste catalyst increased significantly from 85% to about 97%, this is due to the incomplete adsorption of nickel metal by the trapping agent and the increase of slag viscosity in the short melting time stage, resulting in a smaller nickel metal content in the alloy phase and a high nickel metal content in the slag phase, so the recovery of nickel metal is relatively low, and when the melting time reached 4 h, the recovery of nickel metal increased to about 98%, and further increase of the melting time resulted in a small increase in the recovery of nickel metal. Under the conditions of melting temperature of 1500 ℃, melting time of 4 h, iron trapping agent addition of 12%, and carbon reducing agent addition of 4%, the recovery rate of nickel in the spent catalyst reached 99%, which meets the recovery requirements.

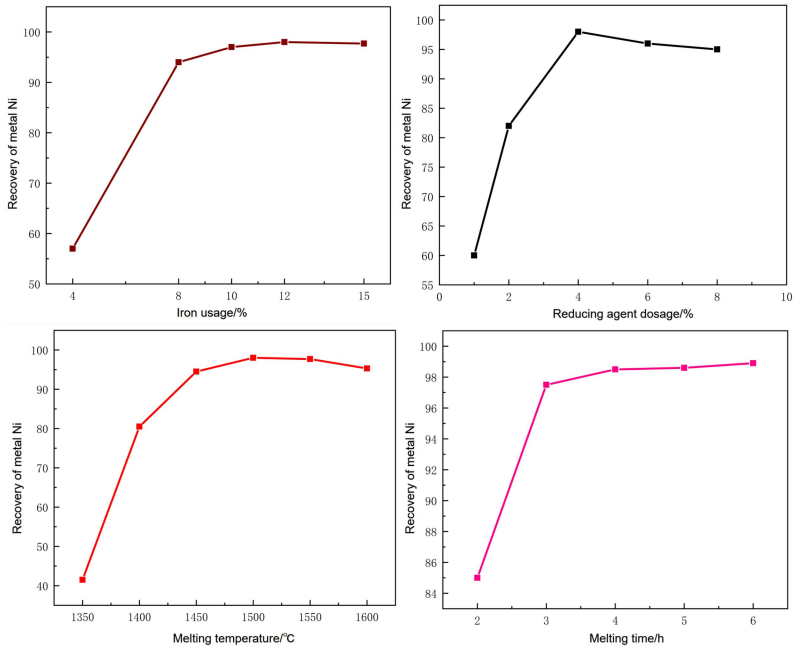

Fig. 4 Influence of variation in nickel recovery as a function of various factors

4. Summary

In this study, the reduction process of selective reduction of nickel-containing waste catalyst with hydrogen was investigated by simulation, and hydrogen reduction and high-temperature melting experiments were carried out, and the following conclusions can be drawn:

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1) Based on the high Fe_2O_3 content in the nickel-containing spent catalyst, hydrogen is used to reduce NiO and iron oxides, and NiO will react rapidly with hydrogen to produce Ni at lower temperatures, and the reduction reaction of Fe_2O_3 is a step-by-step reaction of Fe_2O_3, Fe_3O_4, FeO, and Fe.

2) Under reasonable smelting process parameters, the recovery rate of nickel in the reduced spent catalyst pellet material reaches 99%, which overall achieves the purpose of recovering nickel metal as well as smelting nickel-iron alloy.

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