Research Article

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Recovery of Iron and Zinc from Blast Furnace Dust Using Iron-Bath Reduction

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Abstract: The amount of dust produced from the blast furnace is very large, and this paper proposed a new method for comprehensive utilization of blast furnace dust. Firstly, cold bonded agglomerates directly put into the iron groove were made by blast furnace dust. The cold bonded agglomerates were reduced and melted by the energy of molten iron, and the valuable elements such as Fe reduced into molten iron and zinc existed in rich-Zn dust in the cold bonded agglomerates could be recovered. In order to simulate this process, the reduction behavior of cold bonded agglomerate in the iron bath was studied, and the reduction mechanism were analyzed by Factsage calculation and SEM-EDS. The results showed that: in the slag phase, there were small metallic iron particles dispersed and hard to gather. The main reason for this phenomenon is due to the hindrance role of the carbon residue in the agglomerates, and the problem could be solved through adding magnetite concentrate in cold bonded agglomerates.

Keywords: blast furnace dust; cold bonded agglomerate; carbon residue; iron-bath reduction; smelting-separation

1 Introduction

With the development of the metallurgical industry and improvement of environmental protection awareness, a great deal of attention has been paid to the recovery and treat-

ment of metallurgical dusts. Most of the domestic iron and steel enterprises put the dusts directly back to the iron and steel plant recycling in China. However, due to circulation and enrichment of zinc in the blast furnace, it would shorten the life of lining in a blast furnace and affect the normal operation of the blast furnace [1–4]. At present, there were a number of methods for treating the blast furnace dusts put forward at home and abroad. B. Asadi Zeydabadi leached selectively the valuable elements of the dust by sulfuric acid at low acid concentration and room temperature, and achieved high recovery of zinc. It also could separate zinc and alkali metals from blast furnace flue dust, which zinc as a valuable metal is produced. Secondly, scaffolds and the other similar irregularities in the blast furnaces were controlled [5]. Junwei Han proposed a novel method to recover zinc and iron by reduction roasting-low acid leaching-magnetic separation [6]. Das. B analyzed the characterization, beneficiation and utilization aspects of blast furnace flue dust, blast furnace sludge, LD sludge and LD slag generated at modern steel plants, and the cell or column flotation techniques to recover the carbon values from blast furnace flue dust were used [7]. A. Lopez-Delgado evaluated the use of blast furnace sludge as an adsorbent for the elimination of heavy metal ions from aqueous effluents [8]. Manish Kumar Sinha dealt with the recovery of the zinc and iron from the waste chloride solution of steel industry using solvent extraction and precipitation-stripping process for the synthesis of high purity value added products [9]. However, all of the above methods have not been widely applied in China. So it was a great significance to develop green environmental protection and efficient recycling technology for blast furnace dust.

In this paper, the blast furnace dust was pressed into cold bonded agglomerates using horizontal twinroller machine and then directly put into the simulation device of iron bath, and the metallic oxides would be reduced by carbon in the blast furnace dust using the energy of molten iron. In this way, iron oxides in blast furnace were reduced to metallic iron into molten iron, and zinc oxide was reduced to metallic zinc which would volatilized and collected by the dust remover. Other components entered into slag. It can achieve the purpose of recycling the iron and

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Table 1: Chemical composition of blast furnace dust, %

T_{Fe}	ZnO	C	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Pb	LOI
33.94	3.57	16.30	5.54	1.90	6.52	2.82	1.64	0.92	0.29	13.04

Table 2: Chemical composition of pig iron, %

Fe	Si	Mn	P	S	Ti	V
94.78	0.34	0.21	0.080	0.049	0.124	0.061

zinc in blast furnace dust. This paper also analyzed the reason that the iron and slag did not gather after the high temperature reaction of the cold bonded agglomerates in order to finally realize the effective separation between the iron and slag.

2 Experiment

2.1 Materials

The blast furnace dust and pig iron used in the experiments were provided by a steel company in China. The chemical compositions of them are listed in Table 1 and Table 2, respectively.

It could be found that the content of carbon in the blast furnace dust is high, and it can be the main reducing agent during the reduction of iron and zinc oxide, which means the external carbon is not needed during the reduction process. The iron oxide will be reduced into metallic iron and other compositions will form the slag phase, and the Zn is transformed into steam and volatile to be removed.

2.2 Experimental equipment

The simulation device of iron bath was used as shown in Figure 1. In the experiment, pig iron was put into the crucible. When the furnace was heated to the test temperature, the pig iron melted, which could simulate the situation of the iron groove in front of the blast furnace. The main structures of the device were the heating furnace and temperature controller. The hearth of the furnace was corundum tube, and U-type silicon molybdenum rod distributing around the hearth was as a heating element. The furnace temperature was measured by a double platinum and rhodium thermocouple, and the program is controlled by PID. The maximum temperature of the device was 1873 K and power rating was 8000W.

Figure 1: Simulation device of iron bath (1-Ar gas cylinder; 2-heating furnace; 3-crucible; 4-temperature controller)

2.3 Experimental methods

The blast furnace dust and binder were mixed intensively in a mortar, then pressed into $\Phi 20\text{mm} \times 30\text{mm}$ cylindrical cold bonded agglomerates with water under the pressure of 20 MPa. The addition of binder was 2%. The agglomerates were then dried in a thermostatic oven for 8 hours at 378 K. The crucible with the iron block was placed in the simulation device of the iron bath, then raised the device's temperature to 1773 K and kept for 30min in order to ensure the iron block melt completely. After that, the cold bonded agglomerates were added into the iron bath crucible, and the reaction product was taken out after 1 hour. The proportion of the cold bonded agglomerates was 15% of molten iron. The reaction products were investigated by means of chemical analysis and SEM-EDS analysis. In order to clarify the effect of molten iron composition on the melting effect of the cold bonded agglomerates, the cold bonded agglomerates were added into the crucible directly and reacted at 1773 K to compare the reaction products under the two conditions.

3 Results and Discussions

3.1 Reduction process of cold bonded agglomerates

Figure 2 showed the metallization rate and the zinc oxide content in the agglomerates. It could be seen from Figure 2 that the metallization rate of the cold bonded agglomerates increased gradually with the reaction time prolonged. After the reaction time exceeding to 15 min, the metallization rate decreased and tended to a balance. The content of ZnO in the cold bonded agglomerates was very low, which basically maintained at around 0.001%. In the reduction process, the iron oxide in the cold bonded agglomerates could be reduced to metal iron, and the metallization rate could reach more than 83%, while ZnO could be reduced to metal Zn, which could ensure that the iron recovery rate and removal of zinc [10–14].

Figure 2: Effect of reaction time on the metallization rate and ZnO content of cold bonded agglomerates

Figure 3 demonstrates the morphology of the cold bonded agglomerates reduced in the crucible (a) and in the iron bath (b). The reaction temperature was 1773 K and the reaction time was 30 min.

As shown in Figure 3, it could be seen that the cold bonded agglomerate put directly into the crucible or into the iron bath, the iron oxide in the cold bonded agglomerate could be reduced, but it was still in a dispersed state after reacting for 30 min in the 1773 K condition. There were iron particles attached or mixed to the surface of the cold bonded agglomerate. The iron phase and slag phase were not gathered separately, which was not conducive to the recovery of iron and the formation of slag. Therefore, it is

Figure 3: Morphology of briquetting after reaction

important to analyze the reason of this phenomenon for the efficient handling of blast furnace dust.

3.2 Thermodynamic analysis of molten slag

According to the chemical composition of the blast furnace dust in Table 1, it was assumed that only CaO, MgO, SiO₂ and Al₂O₃ were in the slag phase when the reaction finished. The composition containing the four components was normalized to determine the percentage of each component, and the CaO-MgO-SiO₂-Al₂O₃ quaternary phase diagram was plotted with FactSage [15, 16]. The phase diagram of which was showed in Figure 4.

Figure 4 indicates the melting temperature of the slag phase formed after the reaction of the cold bonded agglomerate exceeds 1873 K. The melting point of the slag was higher, and the temperature of the reduction process can-

Figure 4: Quaternary phase diagram of CaO-MgO-SiO₂-Al₂O₃

Figure 5: Morphology of reaction product containing SiO₂

not reach its melting point, which causes that the cold bonded agglomerate could not melt and still in dispersed state, hindering the aggregation between the iron particles. As a result, the iron phase and slag phase cannot be separated.

From Figure 4 it could be found that if the content of SiO₂ in the slag phase was increased by 4%, the melting point of the slag formed after the briquetting reaction could be reduced to about 1523 K. Therefore, in order to reduce the melting point of the slag phase, 4% of SiO₂ reagent was added. The blast furnace dust and 4% of SiO₂ reagent were mixed intensively in a mortar, then pressed into cold bonded agglomerates. The dried cold bonded agglomerate was placed in an iron bath crucible and reacted at 1500°C for 30 min. Figure 5 shows the morphology of the reaction product.

There was no obvious difference of cold bonded agglomerate that contains SiO₂ or not as shown in Figure 5. The reaction product in the slag phase was dispersed, and it did not gather together. The iron particles were reduced in the middle of the slag phase, which could not achieve the separation of slag iron, recover the valuable element iron in the blast furnace dust. It was not consistent with the results of the four-phase phase diagram analysis of CaO-MgO-SiO₂-Al₂O₃ in Figure 4. So the proportion of the slag-forming phase components in the cold bonded agglomerate was not the main factor affecting the melting and accumulation of the slag in the reaction product.

3.3 Analysis of SEM-EDS

In order to determine the presence state of metallic iron and slag in the reaction product after the high temperature reduction of the cold bonded agglomerate, the reaction product was subjected to SEM-EDS analysis. Figure 6 indicates the morphology and energy spectrum analysis of the Fe phase (a) and slag phase (b) in the reaction product.

Table 1 showed that the content of T_{Fe} of the cold bonded agglomerate is 33.94% and C is 16.30%. According to the reduction of C and iron oxides, the content of C is superfluous to the reduction of iron and zinc oxide. There is still no depletion of residual carbon in the reaction product, as shown in Figure 6.

From Figure 6(a), it could be seen that the iron oxide in the reaction product was reduced at the high temperature, but the metal iron particles were surrounded by the residual carbon in the blast furnace dust. Iron particles were also mixed with unreacted carbon inside resulting in the iron difficult to gather. Because iron particles were lighter, they would only be mixed in the slag phase, floating in the upper part of the molten iron, which affect the recovery of valuable elements in the cold bonded agglomerate. It cannot achieve the purpose of comprehensive utilization of Blast furnace dust.

The energy spectrum analysis results of the mark in Figure 6(b) show that the slag phase which is also wrapped or isolated from the residual carbon in the cold bonded agglomerate is formed by other components, and it cannot be gathered together. The slag phase in the reaction product is macroscopically dispersed and mixed with many of the reduced iron particles.

Figure 6: The morphology and energy spectrum analysis of Fe phase (a) and slag phase (b) of the reaction product

3.4 Validation of results

In order to verify the above points of view, in the course of the experiment, the cold bonded agglomerates were pressed using blast furnace dust and a certain amount of magnetite added to ensure that the carbon could be expended completely. The cold bonded agglomerates contained magnetite concentrate were placed in an iron bath for 30min at 1773 K. Figure 7 shows the morphology of the reaction product.

Figure 7: Morphology of reaction product containing magnetite concentrate

From Figure 7, it can be seen that the reaction product of metallic iron and slag phase were gathered together when the cold bonded agglomerate contained magnetite concentrate, and the slag phase formed a solid phase, which was no longer dispersed. It was conducive to the realization of the separation of iron and slag, and iron could be restored in molten iron easy. Then the goal of recovering the valuable elements in the blast furnace dust would be achieved.

4 Conclusions

- (1) Putting the cold bonded agglomerate into the molten iron, and relying on the heat provided by molten iron, the iron oxide in the cold bonded agglomerate can be reduced into a metal iron in the case of its own carbon as a reducing agent, without an additional reducing agent.
- (2) When the cold bonded agglomerate is directly placed into the molten iron, the reduction of iron ox-

ide cannot completely consume its own carbon, and the reaction product also retains part of the carbon. The reduced iron is still mixed with the slag phase, affecting the recovery of iron.

- (3) Adding a certain amount of high oxidizing materials during the briquetting process of blast furnace dust, the carbon in the blast furnace dust can be completely consumed without any residue after the high temperature reaction. The iron oxide is reduced to metallic iron into the hot metal, and the other components form slag phase which floats on the molten iron, which achieve the separation of iron and slag.

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