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Optimization of the Stainless Steel Dust Briquette Reduction Process for Iron, Chromium, and Nickel Recovery

<https://doi.org/10.1515/htmp-2017-0024>

Received February 25, 2017; accepted December 9, 2017

Abstract: The recovery of iron, chromium, and nickel from stainless steel dust (SSD) has attracted considerable attention for their utilization as secondary resources in the ever-growing field of steelmaking. This paper investigates the reduction process of SSD briquettes in iron-baths in detail in order to determine the optimum processing parameters. A novel method of analysis by studying the erosion behavior of a corundum crucible was adopted to accurately calculate the recovery rate of the metals, and the effect of the parameters on the triple metals recovery rate was determined by orthogonal testing. The results show that the most important factor for the SSD briquetting process is water, followed by sucrose, carbon, and pressure. The optimum parameters of the SSD briquetting process are 13 wt% sucrose, 13 wt% water, 11 wt% carbon, and 30 MPa pressure. The compressive intensity was found to be 27.6 MPa. When a basicity of 1.6, 17% carbon, 5 wt% ferrosilicon, and 6% CaF_2 were used in the SSD briquette reduction process, the triple metal recovery rate was in the range of 94–100 %, 90–100 %, and almost 100 %, respectively.

Keywords: stainless steel dust, orthogonal method, iron, nickel, chromium

Introduction

With the overwhelming demand for stainless steel products in the electrical appliance, medical apparatus, and other industries, the amount of stainless steel

required for these products increases accordingly. To satisfy this growing demand, the increased production of stainless steel, therefore, means that the amount of by-products produced in the steel manufacturing process, like stainless steel dust (SSD), also increases. On an average, the production of 1 ton of steel produces 40–60 kg of dust. In China, 500,000 tons of dust is produced [1], of which electric-arc furnace (EAF) dust and argon-oxygen decarburization (AOD) furnace dust account for 0–2 % and 0.7–1 % of the mass of the molten iron, respectively [2, 3].

A variety of metals such as iron, nickel, and chromium are known to be present in SSD [4–6]. These precious metals can be recovered when SSD is reduced by carbon, and can be reused in the stainless steelmaking process to reduce the requirement of a fresh stock of iron-chromium or iron-nickel alloys.

In previous studies, valuable metals were recovered from SSD usually by two methods. The first was a direct reduction process without briquettes, such as the STAR process [7–11]. The second method used the Inmetco process with an additional briquetting process [12–14], and the metal recovery rate was much higher for the second method than the first. The Fastmet process was found to be very similar to the Inmetco process [15]; however, the chromium recovery rate was much lower. Although both processes efficiently recycled chromium and nickel by doping SSD with carbon, volatilization loss and the permeability of the burdening materials in the carbothermic reduction process can be optimized by briquetting SSD. Kapure et al. [16] used the direct reduction process on low-grade chromite over burden from the Sukinda chromite mines at high temperatures to recover Fe, Cr, and Ni. The effect of the process parameter, such as temperature, time, and reductant, on the recovery of these metals was studied in a laboratory rotary hearth furnace. It was observed that ~90 % Fe and >90 % Ni were recovered within 25 min. Zhang et al. [17–19] discussed the thermodynamics of the reduction process of SSD-bearing carbon briquettes in terms of C-Fe-Cr-O, C-Fe-Ni-O, and C-Fe-

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Ni-Cr-O systems. Peng et al. [6, 8, 20] investigated the reduction kinetics of SSD and carbon pellets, as well as the chromium distribution relationship between slag and nugget. Xue et al. [21–23] proposed an original SSD briquetting process mixed with coal and then discussed the effect of basicity and temperature on their on aggregation behavior. Although their recovery rates on chromium and nickel were very high above researches, the separation of metal nuggets from molten slag was more difficult. In order to solve these problems, Ri et al. [24, 25] discussed the effect of the relationship between basicity, reaction time, and temperature on the extraction of metal nuggets when SSD is briquetted with coal. The results showed that the Fe, Cr, and Ni recovery rate was 92.5%, 92.0%, and 93.1%, respectively. Metal nuggets can be separated easily without using any auxiliary materials because the permeability of the burdening materials significantly influence the metals' recovery rate and reduction reaction kinetics. Wang et al. [26, 27] compared the recovery rates obtained with the direct reduction process and the SSD briquette reduction process. The recovery rates for iron, chromium, and nickel for the SSD briquette reduction process were found to be higher than that for the direct reduction process, because less volatilization loss and much better permeability takes place when the SSD briquettes have a higher compressive intensity. In other words, the compressive intensity of the SSD briquettes is a critical factor that determines the recovery rate of the metals in the subsequent reduction process.

In this article, a novel analysis method for the Fe, Cr, and Ni recovery rate is proposed by the Al_2O_3 balance of the erosion behavior of a corundum crucible. The SSD briquetting and iron-bath reduction processes are systemically discussed, and the parameters

of both processes are optimized by orthogonal experiments.

Experimental process and methodology

SSD briquetting process

The SSD briquetting process mainly consists of burdening, curing, forging, and drying. First, SSD, carbon, and additive agents were weighed for burdening, and then sucrose and water were added for the processes of blending and grinding. The mixed materials were cured at 423 K overnight. Then, 40 g of the mixed materials was adopted for briquetting in a $\Phi 28$ mm mold to obtain the SSD briquettes. The SSD briquettes and their compositions are shown in Table 1. In order to promote the slag melting effect, silicon oxide (CaO/SiO_2) was added to regulate the basicity, while CaF_2 helped to decrease the melting temperature.

SSD briquette iron-bath reduction process

The prepared SSD briquettes and a $\Phi 35 \times 10$ mm iron ingot (99.01% purity) were placed in a corundum crucible and heated by a tube furnace, as seen in Figure 1. The reduction process of the SSD briquettes and iron ingot was carried out over five heating cycles: first, it was heated to 800 °C from the ambient temperature for 3.5 h, followed by increasing the temperature to 1,200 °C for 1.5 h. It was then heated to 1,600 °C for 1.2 h and kept for 40 min. Finally, it was cooled to the ambient temperature for 10 h. In order to increase the chromium recovery

Table 1: Experimental parameters for briquette preparation.

SSDBamount/g	Composition/g					SSDBamount/g	Composition/g				
	SSD	Carbon	SiO_2	CaF_2	Sucrose		SSD	Carbon	SiO_2	CaF_2	Sucrose
36.99	27.77	3.05	2.28	1.11	2.78	37.14	26.88	4.03	0.85	2.69	2.69
36.56	27.70	3.05	1.40	1.66	2.77	37.44	27.75	4.16	0.53	2.22	2.77
37.04	28.02	3.08	0.89	2.24	2.8	36.87	26.49	3.97	2.18	1.59	2.65
36.82	27.70	3.05	0.53	2.77	2.77	36.93	27.55	4.13	1.39	1.10	2.75
37.11	26.65	3.47	2.19	2.13	2.67	37.21	27.58	4.69	0.53	1.65	2.76
37.04	26.83	3.49	1.36	2.68	2.68	37.22	27.74	4.72	0.88	1.11	2.77
37.46	29.06	3.78	0.56	1.16	2.91	36.87	25.95	4.41	1.31	2.60	2.60
37.62	28.46	3.70	0.9	1.71	2.85	37.05	25.87	4.4	2.13	2.07	2.59

Figure 1: Stainless steel dust briquette reduction scheme diagram.

rate, a ferrosilicon reduction agent (74% Si) was added during the fourth stage.

Analysis methodology for the recovery of iron, chromium, and nickel

Because iron, chromium, and nickel nuggets at high temperatures can be oxidized quickly, it will cause a huge deviation in the calculation method for the metal phase. Hence, an original slag phase calculation method needs to be established for calculating the recovery rate. However, the slag amount is hard to obtain for a poor metal/slag separation. Therefore, a mass balance in the SSD briquette reduction process is necessary for analysis in order to calculate the slag amount. SSD briquettes, iron ingots, and ferrosilicon were introduced during the reduction process. Chromium was mainly recovered from the SSD briquettes, while only a small amount was recovered from the iron ingot. Nickel was solely recovered from the SSD briquettes. Gas, slag, and nuggets are outputs. The gas was mainly composed of CO, CO₂, and evaporated ZnO, as well as other oxides such as CaO, SiO₂, MgO, Al₂O₃, and other residue (Fe, Cr, Ni) oxides exist in the slag. Al₂O₃ was produced due to crucible erosion.

It is difficult to determine the slag amount because of the poor separation effect between the nuggets and the slag. However, the slag amount can be derived by Al₂O₃ mass balance. A corundum crucible was used in the reduction process. The weight of the corundum crucible

before the tests, and the total weights of the corundum crucible and slag after the tests were obtained. Equation (1) is derived using the Al₂O₃ mass balance as follows:

$$\begin{cases} m_C + m_S - m_E^A = m_{CS} \\ m_E^A = m_S \times \omega_S^A - m_D \times \omega_D^A \end{cases} \quad (1)$$

where m_C , m_S , m_E^A , m_{CS} , and m_D denote the weights of the crucible, slag, and Al₂O₃ during the erosion process; the total weight of the crucible and slag after tests; and the weight of the dust, respectively. ω_S^A and ω_D^A represent the Al₂O₃ content in slag and SSD.

Equation (2) can be derived through a rearrangement of eq. (1)

$$\begin{cases} m_S = \frac{m_{CS} - m_C - m_D \times \omega_D^A}{1 - \omega_S^A} \\ m_E^A = \omega_S^A \times m_S - \omega_D^A \times m_D \end{cases} \quad (2)$$

Experimental results

Characterization and analysis

For analysis, SSD was obtained from an AOD furnace in a domestic stainless steel plant and then crushed in a pot-mill. A laser particle size analyzer (LS-900) was used to determine the SSD particle size, and the results are plotted in Figure 2. The SSD particle size ranges from 38 μm to 600 μm and follows a typical Gaussian distribution model. Because the particle size distribution has a significant effect on the compressive intensity of the SSD briquettes and the recovery rate, SSD with a particle size ranging from 48 μm

Figure 2: SSD particle size distribution in experiments.

to 270 μm was chosen for this study. Through X-ray fluorescence spectroscopy, the SSD was found to contain 54% Fe_2O_3 , 12.9% Cr_2O_3 , 2.29% NiO , 15.12% CaO , and 4.38% SiO_2 . The Fe, Cr, and Ni-related mineralogical phases mainly consisted of FeCr_2O_4 , NiFe_2O_4 , FeO , and Fe_2O_3 , as determined by X-ray diffraction analysis (Figure 3).

Figure 3: Mineralogical phases in stainless steel dust.

Figure 4 shows the morphology of the SSD as determined by scanning electron microscopy (SEM) (JSM-6301F, JEOL Ltd, Japan). From Figure 4, it is clear that the valuable metals are refined and uniformly dispersed. The technique of magnetic separation for recycling iron, chromium, and nickel is very difficult. Therefore, adopting an SSD briquette iron-bath reduction process could alleviate environmental risks.

Figure 4: Stainless steel dust morphology by SEM tests.

Intensity analysis of SSD briquettes

Figure 5 shows the cylindrical SSD briquette samples. From Figure 5, it can clearly be seen that the surface of the SSD briquette is very smooth and has a good metallic luster. Because the compressive strength has a significant effect on the kinetics of the SSD briquette reduction, the relationship between the compressive strength and curing/drying time has been discussed below.

Figure 5: SSD briquette samples.

The relationship between the compressive strength of the SSD briquette and the drying time is plotted in Figure 6. From Figure 6, it can be seen that up to 1.5 h, the compressive strength increases with the drying time, and the weight loss of SSD briquettes attains a maximum value of 7.2% at that point. After that

Figure 6: Effect of drying time on compressive strength and weight loss of briquettes.

point, the compressive strength stays approximately constant at 26.12 MPa, because the hardness of the briquettes increases with more moisture loss. The compressive strength has a positive relationship with briquette hardness.

The relationship between the compressive strength of the SSD briquette and the curing or briquetting time is plotted in Figure 7. The compressive strength increases with the progress of curing time up to 1.5 h, and then decreases. The maximum compressive strength is 28.36 MPa. The effect of the briquetting time on the compressive strength has a similar relationship as for the curing time. The optimum briquetting time is about 10 min; the maximum compressive strength here is 27.8 MPa.

Figure 7: Effect of curing and briquetting time on compressive strength.

Optimization results for the SSD briquetting process

In order to optimize the SSD briquetting process, orthogonal experiments were conducted, the parameters of which are shown in Table 2. The parameters are mainly the sucrose content, water content, carbon content, and the applied pressure. In the experiments, four factors and three levels of orthogonal testing are investigated. Compressive intensity values were obtained for each experiment.

The results indicate a relationship between the objective and the factor; therefore, the bigger the range of analysis, the bigger influence the factor has. The range analysis results for all factors were

calculated from the orthogonal test results and are shown in Table 3.

From Table 3, it can be seen that the effect sequence of all factors is water > sucrose > carbon > pressure by the value R . The optimum parameters of the SSD briquetting process are 13 wt% sucrose, 13 wt% water, 11 wt% carbon, and 30 MPa pressure. The calculated compressive intensity by range analysis is 27.47 MPa under these conditions, while experiments give a value of 27.603 MPa.

Notably, the effect of carbon and pressure on the compressive intensity is negligible as compared to water and sucrose. Therefore, we can vary the water and sucrose content in order to enhance the compressive intensity during the briquetting process. These results can also be explained by considering that the pressure at the intermolecular level has a critical value; therefore, the compressive intensity decreases when the pressure exceeds that critical value.

Optimization of the SSD briquette iron-bath reduction process

In order to analyze the SSD briquette iron-bath reduction process, orthogonal experiments were carried out, the results of which are shown in Table 5. The parameters are mainly the carbon content, ferrosilicon content, basicity, and CaF_2 content. In the experiments, four factors and four levels of orthogonal testing were designed. The iron, chromium, and nickel recovery rates were calculated by the slag phase for each experiment, as shown in Table 4.

The range analysis results for the SSD briquette iron-bath reduction process can be derived from the parameters in Table 4. The results are shown in Table 5. As for the iron recovery rate, the effect sequence of all factors is basicity > carbon content > CaF_2 content > ferrosilicon content. The basicity has a significant influence on their recovery rate, and the optimum conditions are 15% carbon, 5% ferrosilicon, a basicity of 1.6, and 8% CaF_2 . However, for the chromium recovery rate, the effect sequence of all factors is basicity > carbon content > ferrosilicon content > CaF_2 content, and the optimum conditions are 17% carbon, 5% ferrosilicon, a basicity of 1.6, and 6% CaF_2 .

The range analysis differs between chromium and iron in terms of the carbon and CaF_2 content. Because the chromium and nickel recovery rates are the

Table 2: Optimization results for the SSD briquetting process.

No	SucroseA	WaterB	CarbonC	Pressure/MPaD	Compressive intensity (MPa)
1	1 (7 %)	1 (13 %)	1 (11 %)	1 (20)	21.606
2	1 (7 %)	2 (15 %)	2 (13 %)	2 (30)	17.724
3	1 (7 %)	3 (17 %)	3 (17 %)	3 (40)	15.860
4	2 (10 %)	1 (13 %)	2 (13 %)	3 (40)	22.271
5	2 (10 %)	2 (15 %)	3 (17 %)	1 (20)	19.352
6	2 (10 %)	3 (17 %)	1 (11 %)	2 (30)	17.268
7	3 (13 %)	1 (13 %)	3 (17 %)	2 (30)	27.406
8	3 (13 %)	2 (15 %)	1 (11 %)	3 (40)	23.938
9	3 (13 %)	3 (17 %)	2 (13 %)	1 (20)	20.112

Table 3: Range analysis results for SSD briquetting process.

Level	Sucrose	Water	Carbon	Pressure	Analysis results
K_1	18.40	23.76	20.94	20.36	Main factors:
K_2	19.63	20.34	20.04	20.80	B,A,C,D
K_3	23.82	17.75	20.87	20.69	After
R	5.42	6.01	0.90	0.33	optimization $B_1A_3C_1D_2$

most important for the SSD briquette reduction process, optimization group of chromium takes priority over iron. Therefore, 17% carbon content was used. In order to reduce the risk posed by fluorine ions, the CaF_2 content should be decreased. After careful considerations, the optimized reduction conditions were found to be a

basicity of 1.6, 17% carbon content, 5 wt% ferrosilicon, and 6% CaF_2 .

Conclusions

1. The effect sequence for the SSD briquetting process is water > sucrose > carbon > pressure, and the optimum parameters of the SSD briquetting process are 13 wt% sucrose, 13 wt% water, 11 wt% carbon, and 30 MPa pressure. The compressive intensity is 27.603 MPa under these conditions.
2. When a basicity of 1.6, 17% carbon content, 5 wt% ferrosilicon, and 6% CaF_2 were used, the iron, chromium, and nickel recovery rates were in the range of 94–100 %, 90–100 %, and almost 100 %, respectively.

Table 4: Optimization results for SSDB reduction process.

No	Carbon A	Ferrosilicon B	Basicity C	CaF_2 D	null	Fe	Cr	Ni
1	1 (11 %)	1 (3 %)	1 (1.2)	1 (4 %)	1	97.44	96.51	100
2	1 (11 %)	2 (5 %)	2 (1.6)	2 (6 %)	2	98.31	99.23	100
3	1 (11 %)	3 (7 %)	3 (2.0)	3 (8 %)	3	97.52	95.56	100
4	1 (11 %)	4 (9 %)	4 (2.4)	4 (10 %)	4	94.63	90.69	100
5	2 (13 %)	1 (3 %)	1 (1.2)	3 (8 %)	4	98.76	99.54	100
6	2 (13 %)	2 (5 %)	2 (1.6)	4 (10 %)	3	99.36	99.01	100
7	2 (13 %)	3 (7 %)	4 (2.4)	1 (4 %)	2	94.84	91.68	100
8	2 (13 %)	4 (9 %)	3 (2.0)	2 (6 %)	1	97.47	96.35	100
9	3 (15 %)	1 (3 %)	3 (2.0)	4 (10 %)	2	99.16	97.08	100
10	3 (15 %)	2 (5 %)	4 (2.4)	3 (8 %)	1	97.93	94.14	100
11	3 (15 %)	3 (7 %)	1 (1.2)	2 (6 %)	4	98.49	97.94	100
12	3 (15 %)	4 (9 %)	2 (1.6)	1 (4 %)	3	99.32	99.44	100
13	4 (17 %)	1 (3 %)	4 (2.4)	2 (6 %)	3	95.16	95.58	100
14	4 (17 %)	2 (5 %)	3 (2.0)	1 (4 %)	4	97.23	99.02	100
15	4 (17 %)	3 (7 %)	2 (1.6)	4 (10 %)	1	98.48	99.07	100
16	4 (17 %)	4 (9 %)	1 (1.2)	3 (8 %)	2	99.15	98.23	100

Table 5: Range analysis results for SSD briquette iron-bath reduction process.

	Carbon	Ferrosilicon	Basicity	CaF ₂	Null	Analysis results
$\overline{F}_i^1$	96.975	97.321	98.610	97.208	97.830	For iron: Sequence: C>A>D>B ₂ A ₃ D ₃ B ₂ Optimization group: C
$\overline{F}_i^2$	97.609	98.208	98.718	97.358	97.866	
$\overline{F}_i^3$	98.725	97.333	97.845	98.341	97.840	
$\overline{F}_i^4$	97.505	97.643	95.641	97.908	97.278	
ΔF_i	1.750	0.875	3.078	1.132	0.587	For chromium: Sequence: : C>B>A>D>A ₄ B ₂ D ₂ Optimization group: C
$\overline{F}_i^1$	95.498	97.178	97.923	96.663	96.518	
$\overline{F}_i^2$	96.645	97.850	99.320	97.275	96.555	
$\overline{F}_i^3$	97.150	96.063	97.003	96.868	97.398	
$\overline{F}_i^4$	97.975	96.178	92.023	96.463	96.798	
ΔF_i	2.477	1.672	7.273	0.813	0.880	

Funding: This research was supported by grants from The National Natural Science Foundation of China (No.51304053), Jiangxi University of Science and Technology doctoral start-up fund (No.3401223181).

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