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Recovery of Iron, Chromium, and Nickel from Pickling Sludge Using Smelting Reduction

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Abstract: This paper reports the recoveries of iron, chromium, and nickel from pickling sludge using coal-based smelting reduction. The influences of slag basicity (CaO/SiO₂, which is controlled by high phosphorus oolitic hematite iron ores), reduction temperature, reduction time, and the C/O mole ratio on the recoveries of Fe, Cr, and Ni are investigated systematically. The experimental results show that high recoveries of Fe (98.91%), Cr (98.46%), and Ni (99.44%) are produced from pickling sludge with optimized parameters for the smelting reduction process. The optimized parameters are a slag basicity of 1.5; a reduction temperature of 1550 °C, a reduction time of 90 min, and a C/O mole ratio of 2.0. These parameters can be used as technical support for the recycling of pickling sludge with pyrometallurgy.

Keywords: pickling sludge; high phosphorus oolitic hematite iron ore; coal-based; smelting reduction

1. Introduction

The pickling sludge is produced from pickling wastewater, which comes from the surface treatment of stainless steel, using lime neutralization precipitation technology. The pickling wastewater contains a variety of acids, e.g., HF, H₂SO₄, and HNO₃, as well as different metal ions such as Cr⁶⁺, Cr³⁺, and Ni²⁺. Both the pickling sludge and wastewater seriously affect the surrounding soil and surface water. Therefore, the pickling sludge has been regarded as a toxic waste in the Chinese National Hazardous Waste List, and thus, it should be treated seriously. However, to recycle pickling sludge is very difficult, because it has complicated components and the contents of each component fluctuate significantly (e.g., TFe 13~35%, Cr < 15%, and Ni < 15%). Without any treatment, these components could turn into toxic substances in air or soil, which can pollute the environment. On the other hand, pickling sludge is a valuable renewable resource, because it contains many useful metals such as Fe, Cr, and Ni. In particular, the yield of pickling sludge is about 2,440,500 tons in the world. How to treat pickling sludge is therefore very essential for environmental and resource recycling.

At present, the methods to recycle pickling sludge can be divided into two categories based on treatment processes: pyrometallurgy and hydrometallurgy. With pyrometallurgy, Ma et al. [1], Zhao Jun-xue et al. [2], and Li Qiu-ju et al. [3] adopted carbothermal direct reduction to treat pickling sludge. The valuable metals in the sludge were recovered in the form of alloys. Sun Ying et al. [4] used a carbon reduction-magnetic separation process to recover Fe and Ni from the pickling sludge. The laterite ore tailing was blended into the sludge to improve the recoveries of the metals. The experimental results showed that the best reduction parameters for recovery were a temperature of 1350 °C, a C/O atomic ratio of 1.0, and 25% of pickling sludge. Under this condition, the recoveries of Ni and Fe reached up to 97.86% and 96.07%, respectively. Li Xiao-ming et al. [5,6] used pickling

sludge as a raw material for steel-making or as an auxiliary material for stainless steel production after its desulphurization.

In this paper, we used the pyrometallurgy process to treat pickling sludge and try to recover the elements of iron, chromium, and nickel with smelting reduction, focusing on the optimization of treatment conditions for high recoveries of useful metals. Considering the high content of CaO and CaF₂ in our pickling sludge, high phosphorus oolitic hematite iron ores, which are still unexploited in an industrialized scale and have a high content of SiO₂, are added to control the basicity of the slag during the smelting reduction process. Phosphorus, which exists mainly as apatite [7] in the high phosphorus oolitic hematite iron ores, reacts with CaF₂ in pickling sludge [8,9] to a more stable fluorapatite, avoiding the detrimental element P remaining in ferroalloy. Our study aims to provide technical support for the recycling of pickling sludge by exploring the relation between the element recoveries and process parameters including slag basicity (CaO/SiO₂), reduction temperature and time, as well as the C/O mole ratio.

2. Materials and Methods

2.1. Processes and Methods

The main parameters influencing coal-based smelting reduction are slag basicity (CaO/SiO₂), reduction temperature and time, as well as mole ratio of fixed carbon to reducible oxygen. Pickling sludge, high phosphorus oolitic iron ores, and coals were dried to a moisture content below 5% and then crushed to a particle size of less than 2 mm. The sludge was mixed thoroughly with oolitic iron ores and coals according to specific proportions (see Table 1) by rigorously stirring for approximately 20 min. After that, 100 g mixtures were put into a fused magnesia crucible, weighed by electronic balance (JE1002, Shanghai Puchun Measuring Instrument Manufacturing Co., Ltd., Shanghai, China). The reduction process was performed in a high-temperature molybdenum silicide bar electric furnace (SXL-1700C, Shanghai Jvjing Precision Instrument Manufacturing Co., Ltd., Shanghai, China) with a highest temperature of 1700 °C, in which the temperature fluctuation was controlled within an error of 5 °C. When the furnace was preheated to the required temperature, the crucible was put into the furnace rapidly. After a given time, reduced samples were taken out rapidly and placed in an inert gas atmosphere immediately and then cooled to room temperature rapidly. In addition, smelting reduction experiments were run in air. Samples for testing were obtained by separating slags and ferroalloys from reducing materials, and the recoveries of Fe, Cr, and Ni were calculated. The recovery η was calculated by the following formula:

$$\eta = \frac{m_i}{m_0} * 100\% \quad (1)$$

in which m_i is the total mass of i element in ferroalloys and m_0 is the total mass of i element in samples before reduction. Both of them were analyzed using a chemical method.

The constituents in the reduced materials (under optimum reduction conditions) were investigated by X-ray diffraction (XRD, X' Pert PRO, PANalytical B.V., Almelo, The Netherlands) with Cu K α radiation (40 kV, 40 mA) at the scanning rate of 12°/min from 5° to 90°. The chemical composition of the pickling sludge, high phosphorus oolitic iron ore, and reduced materials were determined by chemical analysis (error bar, 0.2 wt%). The morphology and microstructure of the above products were studied using scanning electron microscopy (SEM, Zeiss Supra 55VP, Carl Zeiss AG, Oberkochen, Germany) on the Zeiss Supra 55VP scanning electron microscope. At the same time, the reduced materials composition analysis was carried out by energy-dispersive spectrometry (EDS, Zeiss Supra 55VP, Carl Zeiss AG, Oberkochen, Germany) on an Inca X-ray spectrometer combined with SEM.

Table 1. The percentages of pickling sludge and high phosphorus oolitic hematite iron ore.

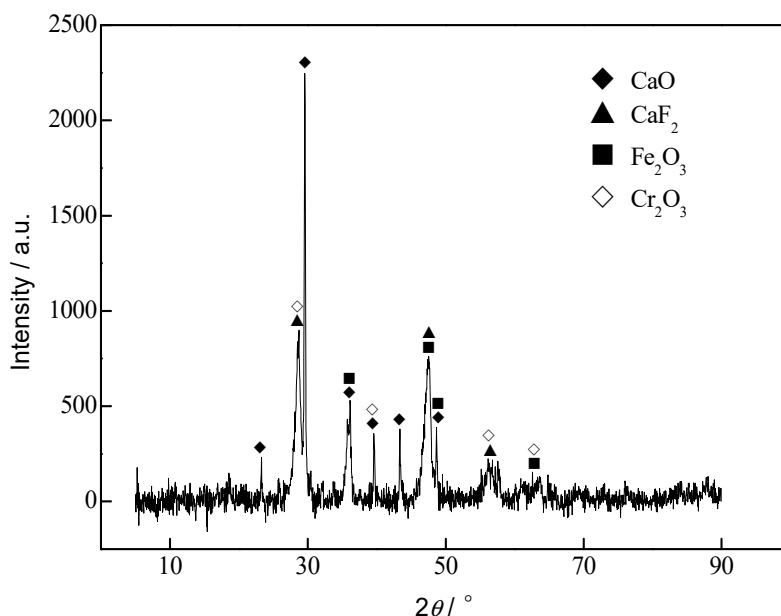
Slag Basicity	Pickling Sludge (%)	High Phosphorus Oolitic Hematite Iron Ore (%)	CaF ₂ (%)
0.5	37.48	62.52	8.77
1.0	65.26	34.74	15.27
1.5	78.78	21.22	18.43
2.0	86.78	13.22	20.31

2.2. Pickling Sludge

The chemical composition of the pickling sludge after drying at 105 °C is given in Table 2. The contents of the useful metals are total iron (TFe) 15.36 wt%, Ni 0.65 wt%, and Cr 4.72 wt%. The other main components are CaF₂ (23.4 wt%) and CaO (12.62 wt%), and the remaining oxides are relatively low. The dominant phases (CaO, CaF₂, Fe₂O₃, and Cr₂O₃) can be confirmed by XRD, as shown in Figure 1.

Table 2. Chemical composition of pickling sludge after drying at 105 °C (mass fraction, wt%).

TFe	Cr	Ni	P	S	CaO	CaF ₂	MgO	SiO ₂	Al ₂ O ₃
15.36	4.72	0.65	0.06	2.43	12.62	23.4	2.05	3.32	2.83

**Figure 1.** XRD pattern of pickling sludge after drying at 105 °C.

2.3. High Phosphorus Oolitic Iron Ore

Samples of high phosphorus oolitic iron ores collected from Wuhan Iron and Steel (Group) Corporation, China, were used. The chemical composition and XRD of the ores are given in Table 3 and Figure 2. TFe is 42.21 wt%, and Fe exists mainly in the form of a hematite. SiO₂, which is detrimental to the iron recovery, is relatively high (21.8 wt%).

Table 3. Chemical composition of high phosphorus oolitic iron ore (mass fraction, wt%).

TFe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	P	S	K	Mn
42.21	4.31	21.80	5.47	4.33	0.59	0.19	1.31	0.13	0.41	0.20

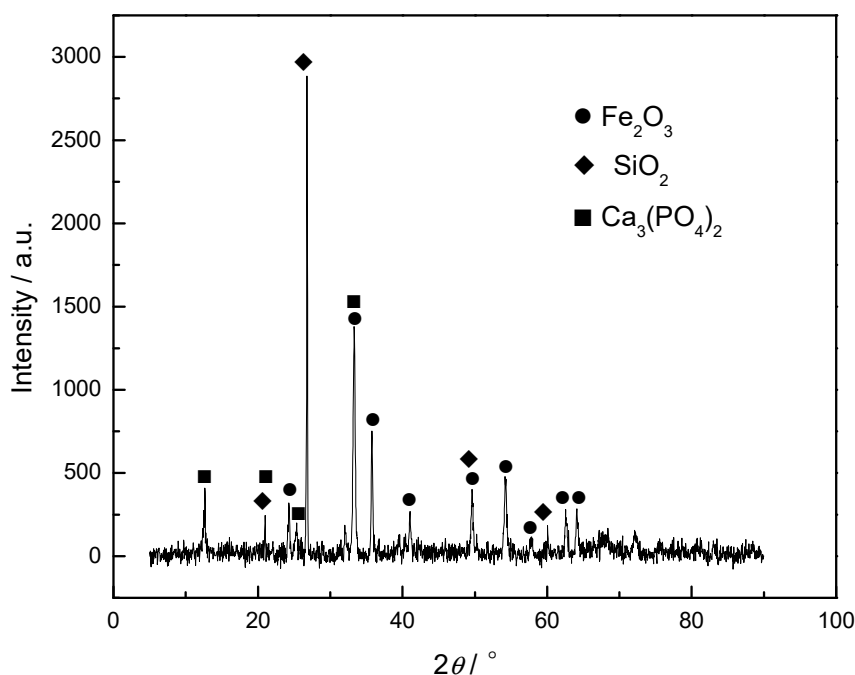


Figure 2. XRD pattern of high phosphorus oolitic iron ore.

2.4. Reductant

The anthracite coal was used as reductant. The contents from a proximate analysis are listed in Table 4, which shows that the coal has a high level of fixed carbon (FC_{ad}) and low level of water (M_{ad}), ash (A_{ad}), volatile (V_{ad}), sulfur (S), and phosphorus (P). It is considered a good reductant for smelting reduction.

Table 4. Proximate analysis of the coal (mass fraction, %).

FC_{ad}	V_{ad}	A_{ad}	M_{ad}	P	S
67.83	18.45	12.02	1.48	0.004	0.028

3. Results

3.1. Effect of Slag Basicity on Metals Recoveries

The relationship between slag basicity and the percentages of pickling sludge and high phosphorus oolitic hematite iron ore is shown in Table 1, which shows that the percentages of pickling sludge increase gradually with the increase of slag basicity.

Suitable slag basicity (CaO/SiO_2) and an excess of CaF_2 are beneficial to the reduction of metal oxides and high recoveries of metals by suppressing the formation of difficult reduction materials such as Fe_2SiO_4 , $NiFe_2O_4$, and $FeCr_2O_4$, and increasing the fluidity of slags [10–15]. Therefore, in our study, a series of experiments were carried out on various slag basicities (CaO/SiO_2) and CaF_2 contents, which were controlled by the amount of high phosphorus oolitic hematite iron ore. The main purpose is to determine the synergy impacts on the recoveries of Fe, Cr, and Ni; therefore, we fixed the other conditions as follows: reduction temperature, 1500 °C; reduction time, 90 min; and mole ratio of C/O, 2.0. Figure 3 presents the recoveries of Fe, Cr, and Ni as a function of slag basicity. It is clear that the recoveries increase gradually with increasing slag basicity, which is significantly effective for the recovery of Cr. During the reduction process, slag basicity increases gradually with the increasing percentages of pickling sludge and CaF_2 (Table 1). CaF_2 improves the fluidity of slag, which benefits the growth of fine liquid-ferroalloy particles and promotes the separation of slag and ferroalloy [13]. The recovery of Cr increases from 92.59% to 98.18%, and Fe and Ni increase from 97.85% to 99.01%, and

from 98.14% to 99.03%, respectively, as the slag basicity increases from 0.5 to 2.0. However, a further increase in slag basicity results in slight decreases in both Fe and Ni recoveries, when the slag basicity is 1.5. Considering that a higher slag basicity needs more pickling sludge and produces more slag, which has a higher consumption energy and a longer reduction time for the aggregate and growth of fine liquid-ferroalloy particles, it is appropriate to control the slag basicity of 1.5 in the experimental process. When the slag basicity is 1.5, the recoveries of Fe, Cr, and Ni are still as high as 98.75%, 96.32%, and 98.98%, respectively.

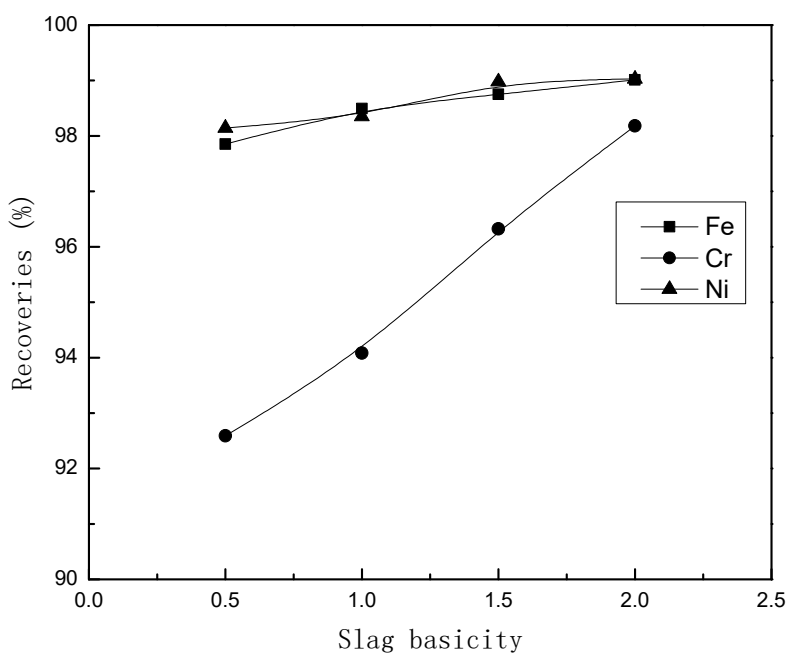


Figure 3. Effect of slag basicity on metals recoveries.

3.2. Effect of Reduction Temperature on Metals Recoveries

To determine the optimal reduction temperature, the smelting reduction was carried out at various temperatures between 1400 and 1600 °C. The other process parameters are slag basicity of 1.5; reduction time of 90 min; and mole ratio of C/O, 2.0. The effect of temperature on the recoveries of Fe, Cr, and Ni is shown in Figure 4. When the reduction temperature increases from 1400 to 1550 °C, the recoveries of Fe, Cr, and Ni increase from 87.77% to 98.91%, from 79.23% to 98.46%, and from 96.53% to 99.44%, respectively, but level off above 1550 °C. The temperature significantly affects the recovery of Cr, followed by that of Fe and Ni. Many studies [11,16,17] showed that the reduction temperatures for Fe₂O₃, Cr₂O₃, and NiO are lower than 1300 °C. However, this temperature is too low for Fe, Cr, and Ni metal grains to aggregate and mature. Basically, the Fe-Cr-Ni alloy particles are formed by nucleation, crystal growth, grains merger, formation of fine liquid-ferroalloy particles by carburizing, and the aggregation and growth of fine liquid-ferroalloy particles [18,19]. The temperature in this smelting reduction process is mainly to reduce the viscosity of slag. This increases the aggregation and the growth speed of fine liquid particles of the Fe-Cr-Ni. On the other hand, separating ferroalloy from slag is mainly determined by the size, shape, and state of existed ferroalloy particles. The liberation degree to separate ferroalloy from slag is higher in coarser particles of ferroalloy and so are the recoveries of Fe, Cr, and Ni. If the ferroalloy particles are too small, the ferroalloy and slag can be wrapped together and the liberation degree will be low, which will influence the effective separation of ferroalloy and slag. Therefore, based on these observations, a reduction temperature of 1550 °C might be the optimized temperature in the reduction process.

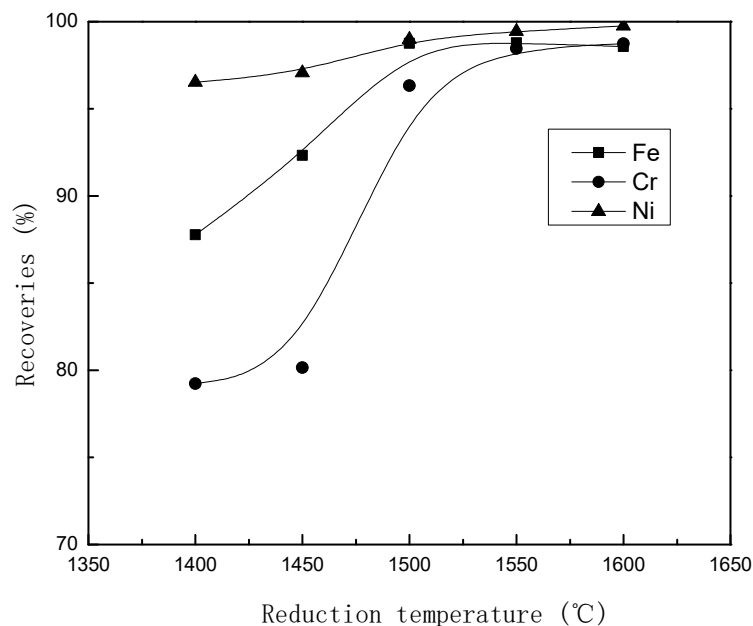


Figure 4. Effect of reduction temperature on metals recoveries.

3.3. Effect of Reduction Time on Metals Recoveries

To optimize the reduction time, a series of reduction tests was performed at various times. Other parameters such as the slag basicity (1.5), reduction temperature (1550 °C), and the mole ratio of C/O (2.0) were kept. The effects of reduction time on the recoveries of Fe, Cr, and Ni are presented in Figure 5. For all elements, the recovery increases with increasing reduction time but levels off after 90 min. When the reduction time is 90 min, the recoveries of Fe, Cr, and Ni are 98.91%, 98.46%, and 99.44% respectively. The effect is most significant on the recovery of Cr, followed by Fe and Ni, similar to the effect of temperature. The increase of the recoveries is mainly due to the increase of the number of larger ferroalloy particles, which arise from the longer time allowed for aggregation of the fine liquid-ferroalloy particles. After 90 min, the process increases the consumption energy but does not significantly increase the recoveries; thus, we consider this time period to be optimum for reduction.

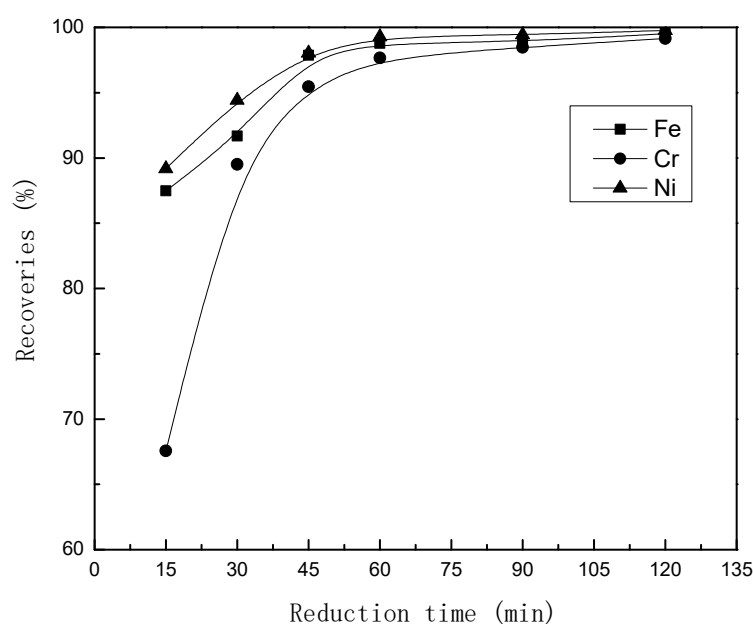


Figure 5. Effect of reduction time on metals recoveries.

3.4. Effect of C/O Mole Ratio on Metals Recoveries

To investigate the optimum amount of coals, the effect of C/O mole ratio on the recoveries of Fe, Cr, and Ni was studied under the following conditions: slag basicity of 1.5; reduction temperature of 1550 °C; and reduction time of 90 min. The value of C/O mole ratio varies from 0.5 to 2.5. Figure 6 shows the results. The recoveries of Fe, Cr, and Ni increase rapidly with an increase of the C/O mole ratio from 0.5 to 2.0 but change insignificantly when the C/O mole ratio is beyond 2.0. Again, the effect of C/O mole ratio is more effective on the recovery of Cr, followed by Fe and Ni. Generally, the suited C/O mole ratio is around 1.1; however, in our experiment, as the C/O mole ratio increases from 1.0 to 2.0, the recoveries of Fe, Cr, and Ni still increase (Figure 6). We attribute that to the presence of CaSO_4 in the pickling sludge, and that reducing CaSO_4 by carbon consumes carbons. Therefore, we need excess carbons. Additionally, chromium carbide forms in the process, which is beneficial to the reduction of chromium trioxide [16]; thus, a C/O mole ratio of 2.0 is recommended.

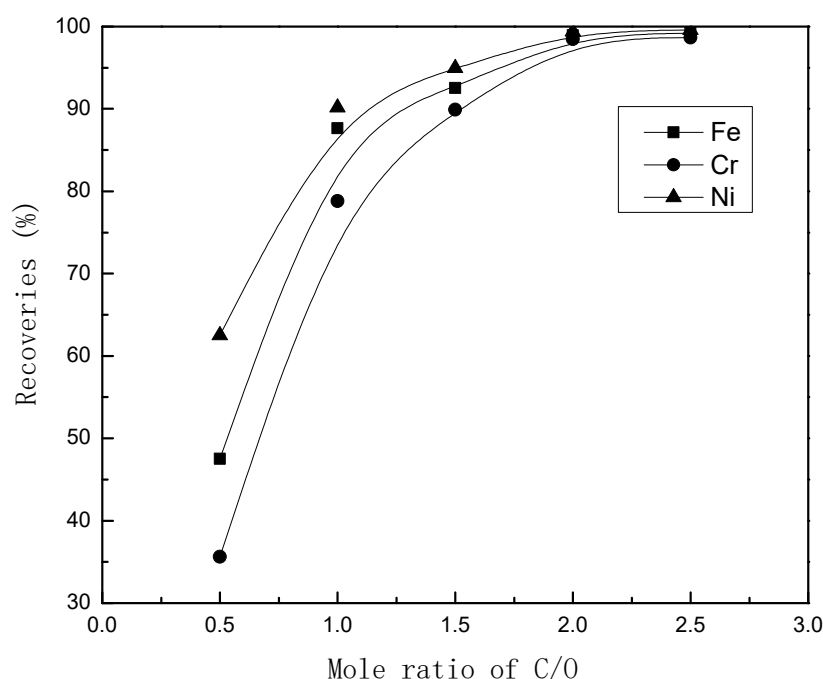


Figure 6. Effect of C/O mole ratio on metals recoveries.

4. Discussion

4.1. The Macro-Morphology and Chemical Composition of Ferroalloy

Under the experimental condition with all optimum parameters of slag basicity of 1.5, reduction temperature at 1550 °C, reduction time of 90 min, and C/O mole ratio of 2.0, ferroalloy products were obtained. The macro-morphology of the ferroalloys is shown in Figure 7, and the chemical composition is given in Table 5. The ferroalloys are droplet-shaped with metallic luster. In Table 5, the main constituents are TFe (74.85 wt%), Cr (6.61 wt%), Ni (1.95 wt%), and C (6.02 wt%). The contents of detrimental elements of P and S are 0.3 wt% and 0.032 wt%, respectively.



Figure 7. The macro-morphology of ferroalloy particles.

Table 5. Chemical composition of ferroalloy (mass fraction, wt%).

TFe	Cr	Ni	P	S	C
74.85	6.61	1.95	0.3	0.032	6.02

4.2. XRD Analysis of Ferroalloy

XRD of the ferroalloys prepared under the optimum experimental condition is given in Figure 8, which shows that the main phases are Fe, Fe_3C , and Cr_7C_3 .

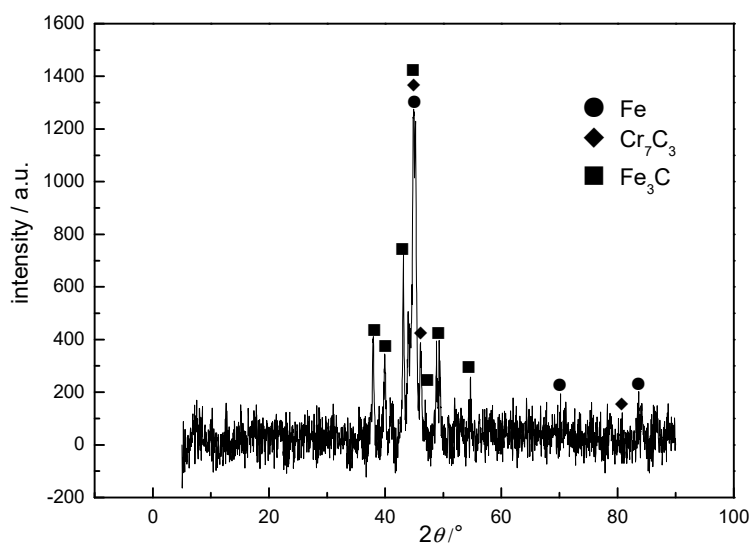


Figure 8. XRD pattern of ferroalloy.

4.3. SEM and EDS Analysis of Ferroalloy

Figure 9 shows the SEM images of the reduced products. The spectra of EDS measurements at different points and the index for different elements are also presented. There are different phases with clear phase boundaries. The elemental analysis showed the dominance of Fe, Cr, C, Ni, and some ignorable elements such as P and S. The grey phase contains more Cr than the lighter and darker phases.

The EDS measurements confirmed that the oxides of Fe_2O_3 , Cr_2O_3 , and NiO in the pickling sludge were reduced to Fe, Cr, and Ni in the form of ferroalloys, showcasing the recycling of pickling sludge.

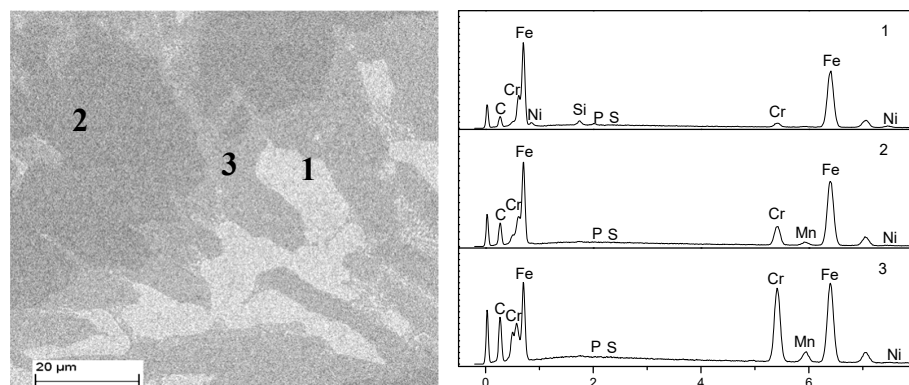


Figure 9. Scanning electron microscope (SEM) and energy-dispersive spectrometry (EDS) analysis results of ferroalloy.

4.4. Analysis of Ferroalloy Particle Aggregation and Growth Mechanism

Carburizing Fe and Cr reduces the melting point of ferroalloys, and a lot of fine liquid-ferroalloy particles are produced during the smelting reduction. The diameter of such particles (containing Fe-Cr-Ni-C) is very small, and the particles have large interfaces and interface energy, G , which can be calculated from liquid ferroalloy particles and molten slags, J , by

$$G = \sigma_{m-s} * S \quad (2)$$

in which σ_{m-s} is the interfacial tension between the liquid ferroalloy particle and molten slag, N/m; S is the contact area in m^2 . According to the principle of minimum free energy, the particle growing process can only occur spontaneously when the energy change in the process is less than 0, i.e., $dG < 0$ and $\sigma_{m-s} > 0$ in Equation (2). Then, both fine liquid-ferroalloy particles and molten slags have the tendency to shrink the surface, and the fine liquid phase of Fe-Cr-Ni-C alloy particles gradually aggregates and increases.

The aggregation and growth of fine liquid-ferroalloy particles decrease the interfacial free energy. In the first stage of the smelting reduction, a large number of fine liquid-ferroalloy particles form. The flow of molten slag causes the migration of these fine particles, which promotes the fine particles to merge into large particles. With further smelting reductions, more fine liquid-ferroalloy particles form and merge, and the number of large ferroalloy particles gets bigger and bigger. This beneficially coincides with the separation of ferroalloy from slags, leading to the enhancement of the recoveries of Fe, Cr, and Ni.

The aggregation and growth of fine liquid-ferroalloy particles are related to the interfacial tension between fine liquid-ferroalloy particles and molten slags (σ_{m-s}/η_s), as well as the viscosity of molten slag (η_s), which can be expressed by the ratio σ_{m-s}/η_s [20–22]. A larger ratio means that the aggregation and growth of fine liquid-ferroalloy particles are more easily achieved. σ_{m-s} is related to the surface tension and contact angle of molten slag and liquid ferroalloy, which is generally constant in a large range of temperatures. Obviously, in this case the viscosity of molten slag η_s plays a key role in the formation of ferroalloy particles. Because CaF_2 is strongly basic and surfactant, it can effectively reduce the slag viscosity η_s . A lower η_s is then expected with an increase in slag basicity and pickling sludge, and thus higher recoveries of Fe, Cr, and Ni.

5. Conclusions

The process parameters to recover valuable metals from pickling sludge through smelting reduction have been studied systematically with anthracite coals as a reductant and high phosphorus oolitic hematite as a modifying agent on the basicity of slag. According to our study, the following conclusions can be drawn:

- (1) The recoveries of Fe, Cr, and Ni of 98.91%, 98.46%, and 99.44%, respectively, have been obtained under the optimal condition of a slag basicity of 1.5, a reduction temperature of 1550 °C, a reduction time of 90 min, and a C/O mole ratio of 2.0.
- (2) The Fe_2O_3 , Cr_2O_3 , and NiO in the pickling sludge were reduced to Fe, Cr, and Ni, by smelting reduction, in the form of ferroalloys, seamlessly achieving the recycling of the pickling sludge.

Author Contributions: Z.T. and X.D. conceived and designed the experiments; Z.T., X.Y., and Y.D. analyzed the data and wrote the paper; and Z.T., Y.D., and C.L. finished the experiments.

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Conflicts of Interest: The authors declare no conflict of interest.

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