

Article

Dephosphorization Behavior of High-Phosphorus Oolitic Hematite-Solid Waste Containing Carbon Briquettes during the Process of Direct Reduction-Magnetic Separation

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Abstract: In this paper, the process of direct reduction roasting using magnetic separation to produce direct reduction iron (DRI) from high-phosphorus oolitic hematite, using coal slime and blast furnace dust as reductant, is investigated. The possible use of slime coal and blast furnace dust as reductant and the dephosphorization behavior during the process of direct reduction was studied. Experimental results showed that both blast furnace dust and coal slime can be used as reductant under certain conditions in the process. The dephosphorization mechanism of blast furnace dust and coal slime were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM)-energy dispersive X-ray spectroscopy (EDS). A DRI with 91.88 wt. % iron grade, 88.38% iron recovery and 0.072 wt. % P can be obtained with 30 wt. % blast furnace dust as reductant. The program not only used blast furnace dust but also recovered iron from blast furnace dust and high-phosphorus oolitic hematite. The analysis results revealed that phosphorus is distributed in gangue mineral and fluorapatite when blast furnace dust is used as reductant. Phosphorus-bearing minerals were not reduced to phosphorus element when the blast furnace dust was the reductant, but part of the fluorapatite reduced to phosphorus which smelt into metallic iron with coal slime as reductant. This led to a high phosphorus content of DRI. This research could provide support to the idea concept for recycling of carbon-containing solid waste and to assist the effective recovery of refractory iron ore by direct reduction–magnetic separation.

Keywords: dephosphorization; blast furnace dust; coal slime; high-phosphorus oolitic hematite; DRI

1. Introduction

Heavy dependence upon imported iron ore concentrates is one of the most significant challenges for China's pyrometallurgical industry. In China, high-phosphorus oolitic hematite constitutes approximately 11.1% of iron reserves, hence the application of recovering these refractory ores can be considered based on current situation [1]. However, the intimately intermixed structural unit of both fluorapatite and chamosite in high-phosphorus oolitic hematite have caused huge difficulties in obtaining the qualified iron ore concentrates by conventional methods of mineral processing [2,3]. A coal-based direct reduction roasting process combined with magnetic separation operation [4–7] has been developed by using carbon-containing pellets of high-phosphorus oolitic hematite with coal

as reductant to treat the refractory ore in recent years. In this process, the iron oxide is first reduced to a metallic iron in the roasted products also known as briquettes. The briquettes are ground and concentrated by magnetic separation to obtain direct reduction iron (DRI). The DRI, containing more than 90 wt. % Fe grade, 80% Fe recovery rate and less than 0.1 wt. % P-content, is expected to be a substitute of steel scrap in electric arc furnaces (EAF) for steelmaking. It is well known that the phosphorus content of the feed stock for steelmaking must be strictly controlled because too high phosphorus content will cause cold brittleness and reduce the ductility brittleness of steel [8–10].

It should be stressed that the cost of coal as reductant is one of the affecting factors of the economic result of this new technique. In fact, both coal slime and blast furnace dust are considered to be a by-product in the coal washing process of the coal industry and the ironmaking process of the metallurgical industry, respectively. Coal slime and blast furnace dust all contain solid carbon as reductant in the direct reduction process, and they have not received effective use at the research stage due to high ash content and complex components [11–14]. Meanwhile, since the properties of the blast furnace dust and coal slime differ from coal, the dephosphorization of this process may differ from the coal's dephosphorization process that was noted above [5,6], and have a higher receptivity on reductant type from the viewpoint of phosphorus content of DRI.

In this work, high-phosphorus oolitic hematite was treated with direct reduction followed by magnetic separation process with solid waste containing carbon as reductant. Also, the dephosphorization behavior of this process was investigated by XRD and SEM-energy dispersive X-ray spectroscopy (EDS) analysis.

2. Experimental Details

2.1. Materials

The high-phosphorus oolitic hematite [15] was obtained from Hubei province, China, containing 42.72 wt. % Fe, 17.90 wt. % SiO₂, 9.35 wt. % Al₂O₃, 3.58 wt. % CaO, and 0.79 wt. % P. The valuable Fe-containing minerals are hematite, a small amount of limonite, magnetite, and pyrite. The 97.82% of Fe existed in hematite and limonite. The main gangue minerals were quartz, fluorapatite and chamosite. 80.74% phosphorus is distributed in the form of fluorapatite, and detailed characteristics of the raw iron ore are shown in Table 1 and Figure 1.

Table 1. Chemical analysis results of high-phosphorus oolitic hematite.

Components	T·Fe	SiO ₂	Al ₂ O ₃	MgO	CaO	SO ₃	P
Content (mass/%)	42.72	17.90	9.35	0.59	3.58	0.12	0.79
Components	TiO ₂	V ₂ O ₅	SrO	K ₂ O	MnO	As ₂ O ₃	
Content (mass/%)	0.20	0.08	0.02	0.65	0.20	0.02	

The basicity is calculated: $(\% \text{CaO} + \% \text{MgO}) / (\% \text{SiO}_2 + \% \text{Al}_2\text{O}_3) = (3.58\% + 0.59\%) / (17.90\% + 9.35\%) = 0.15$, which is less than 0.5, so it is considered to be acid high-phosphorus iron ore [16].

The XRD analysis result in Figure 1 indicated that the major valuable mineral component of high-phosphorus oolitic hematite was hematite, and the main gangue minerals were quartz and chamosite, among which phosphorous mainly existed in fluorapatite, as per JCPDS file no. 79-1741, 85-0789, 85-1356, and 76-0558 respectively. The SEM (Carl Zeiss, Jena, Germany) illustrated that the center of the oolite particle was quartz, and the structure of high-phosphorus oolitic hematite was concentric ring bands. The hematite and chamosite co-occurred with each other in alternating layers in the form of concentric rings. Hematite and gangue minerals (chamosite and fluorapatite) were associated with cemented uneven ring boundaries. Fluorapatite was irregular and closely associated with hematite. This shows why the traditional sorting methods, such as bioleaching, magnetizing, and roasting for dephosphorization mentioned earlier are difficult [2,3].

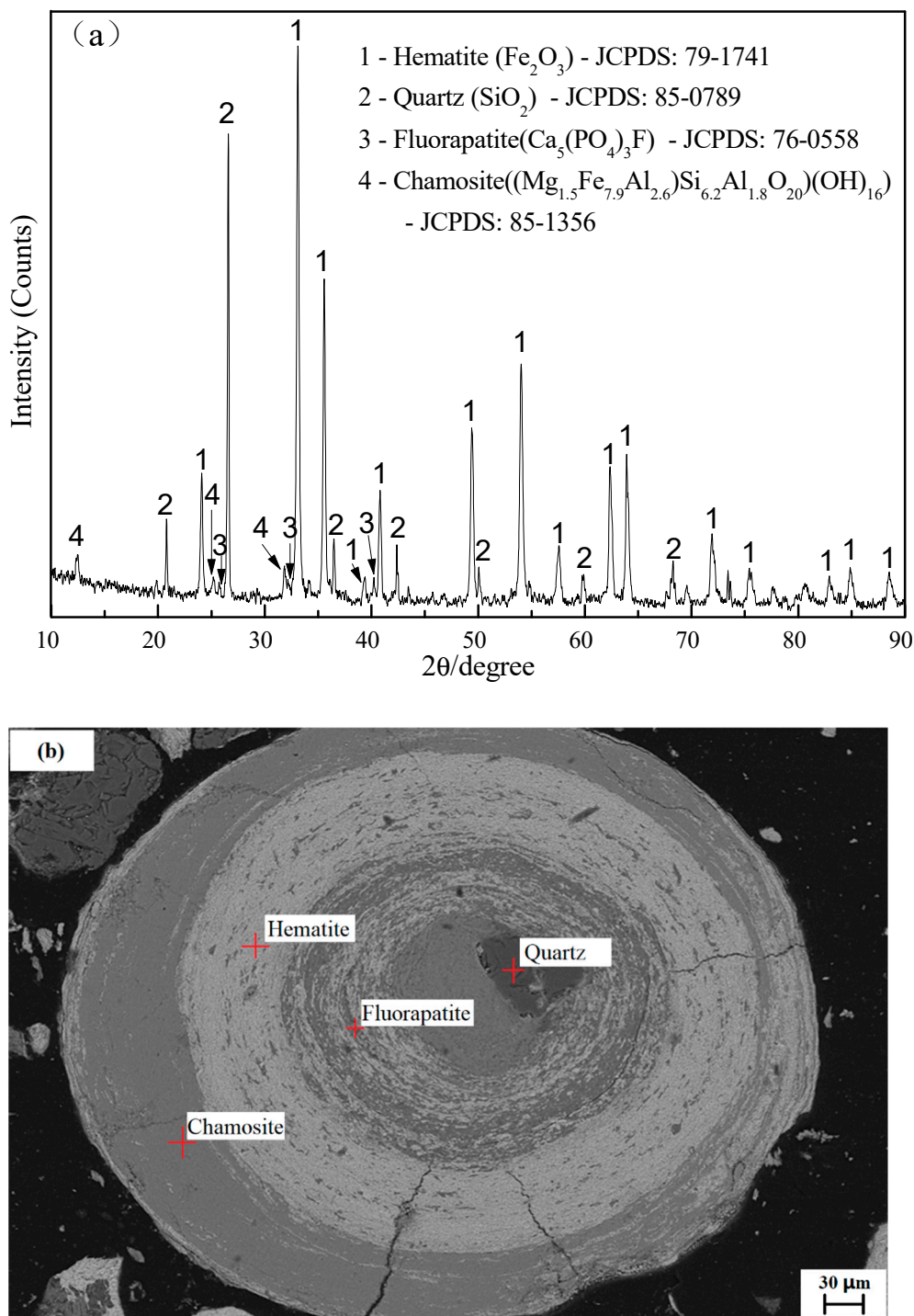


Figure 1. Results for high-phosphorus oolitic hematite. (a) XRD analysis result with JCPDS; (b) SEM image. JCPDS: Joint Committee on Powder Diffraction Standards.

The iron ore used in the experiments was crushed to 100% passed 2 mm. Blast furnace dust and two kinds of coal slime with different silica content were used as reductants, respectively (for their proximate analysis results, referred to Table 2), and their granularity used in the experiments was 100% passed 0.15 mm.

Table 2. The proximate analysis and SiO₂ content of different kinds of reductants.

Reductant	Code	Proximate Analysis (wt. %)			SiO ₂ (mass/%)
		V _d	FC _d	A _d	
Blast furnace dust	R ₁	9.08	33.82	57.10	7.68
Coal slime 1	R ₂	26.75	43.52	29.73	13.56
Coal slime 2	R ₃	29.25	40.97	29.78	20.33

Note: M: moisture, A: ash; V: volatiles, FC: Fixed Carbon; d: In coal sample analysis dry-basis leaves out all moistures, including surface moisture, inherent moisture, and other moistures while ad (air-dried basis) neglects the presence of moistures other than inherent moisture. Therefore, $V_d = V_{ad} / (100\% - M_{ad}\%)$, $FC_d = FC_{ad} / (100\% - M_{ad}\%)$, $A_d = A_{ad} / (100\% - M_{ad}\%)$.

The proximate analysis result of blast furnace dust was 57.10 wt. % A_d, 33.82 wt. % FC_d, and 9.08 wt. % V_d. The T·Fe of the blast furnace dust conducted by a laboratory of China University of Geosciences (Beijing) was 23.96%. Evidently, blast furnace dust contained considerably lower volatile content and higher ash content than coal slime 1 and 2. The proximate analysis result illustrated two kinds of coal slime had roughly the same composition. The content of SiO₂ was different among the three kinds of reductants.

2.2. Experimental Procedure

Volatiles of reductants have reductive effect in the direct reduction process [17]. Therefore, the reductant dosage was used in these experiments instead of the mole ratio of the fixed carbon to removable oxygen of the iron oxides (C/O ratio). The reductant dosages were 20 wt. % and 30 wt. % respectively, and these dosages referred to the weight ratio of the raw iron ore. 20 g of raw iron ore was thoroughly mixed with a different dosage reductant and an identical amount of the additives (20% CaCO₃, 2.5% Na₂CO₃) [18]. A mixture of raw ore, reductant, and additives with a mass ratio of 100:(different dosages reductant):22.5 was used throughout the study. (i.e., 20 wt. % R₁ was a mixture of raw ore, reductant, and additive with a mass ratio of 100:20:22.5). The mixture was put in the graphite crucible of 65 mm in diameter and 70 mm in height. The graphite crucible was put into a muffle furnace with a temperature programmer for reduction roasting at 1150 °C for 60 min to obtain a roasted product called a briquette. The air-cooled briquettes were ground to −0.043 mm powder of more than 80% after the two-stage grinding. The powder was finally put in the XCGS-73 magnetic separator with magnetic field strength of 87.58 kA/m to separate the material. The magnetic product obtained after magnetic separation is called DRI. The grinding experiments were conducted in a rod mill with a speed of 192 r/min (RK/BM-1.0L, Wuhan Rock Crush & Grind Equipment Manufacture Co., Ltd., Wuhan, China) with ten Φ15 mm × 120 mm rods at 60 wt. % solid density. The XCGS-73 magnetic separator was used in the magnetic separation process.

2.3. Analysis and Characterization

The chemical analyses results were generated [19–22] by the China University of Geosciences (Beijing) Analytical Laboratory. The main evaluation indices of experimental results were iron grade (% T·Fe), phosphorus content [% P] and iron recovery rate. $\varepsilon_{bfd(Fe)}$ is iron recovery when R₁ is the reductant Equation (1). $\varepsilon_{(Fe)}$ is iron recovery when R₂ and R₃ are the reductant Equation (2), respectively. The elemental content of the reduced products was analyzed by a scanning electron microscope (Carl Zeiss EVO18, Jena, Germany) equipped with an EDS detector (Bruker XFlash Detector 5010, Jena, Germany). SEM images were recorded in backscatter electron mode operating in low vacuum mode at 20 kV. XRD patterns were obtained using a diffractometer (Rigaku D/Max 2500, Tokyo, Japan) under the following conditions: Cu Kα radiation 150 mA tube current, 40 kV voltage of 10° to 90° scanning range, and 5°/min scanning speed.

$$\varepsilon_{bfd(Fe)} = \frac{W_3 \times \beta_3}{W_1 \times \beta_1 + W_2 \times \beta_2} \times 100\% \quad (1)$$

$$\varepsilon_{(Fe)} = \frac{W_3 \times \beta_3}{W_1 \times \beta_1} \times 100\% \quad (2)$$

W_1 = weight of raw iron ore; β_1 = iron grade of raw iron ore; W_2 = weight of R_1 ; β_2 = iron grade of R_1 ; W_3 = weight of DRI; β_3 = iron grade of DRI.

3. Results and Discussions

3.1. Measurement of Reduction and Separation Results

The experimental results for the direct reduction of R_1 , R_2 and R_3 as reductant respectively in the phosphorus removal of briquettes during direct reduction roasting—magnetic separation are shown in Figure 2.

Figure 2 illustrates that the DRI with different iron grade, phosphorus content and iron recovery rate were obtained. These results indicate that R_1 , R_2 , and R_3 can be used as reductant under certain conditions in the direct reduction roasting. As shown in Figure 2, the β_3 of the DRI was about 90 wt. % under the appropriate beneficiation conditions. This indicated that the DRI of 72.78% $\varepsilon_{bfd(Fe)}$ and 0.062% P, 88.38% $\varepsilon_{bfd(Fe)}$ and 0.072% P were obtained, when the dosage of R_1 was 20 wt. %, 30 wt. %, respectively. Meanwhile, the DRI of 81.83% $\varepsilon_{(Fe)}$ and 0.076% P, 91.11% $\varepsilon_{(Fe)}$ and 0.17% P were obtained, when the dosage of R_2 was 20 wt. %, 30 wt. %, respectively. The DRI of 79.01% $\varepsilon_{(Fe)}$ and 0.062% P, 90.45% $\varepsilon_{(Fe)}$ and 0.27% P were obtained, when the dosage of R_3 was 20 wt. %, 30 wt. %, respectively. Therefore, these results illustrate that the process of direct reduction roasting-magnetic separation showed the ability to treat high-phosphorus oolitic hematite as low-grade refractory iron ore by removing the phosphorus. The experimental results illustrated different kinds of reductants also had different functions in the dephosphorization process. The more detailed discussion will be provided later in Sections 3.2 and 3.3.

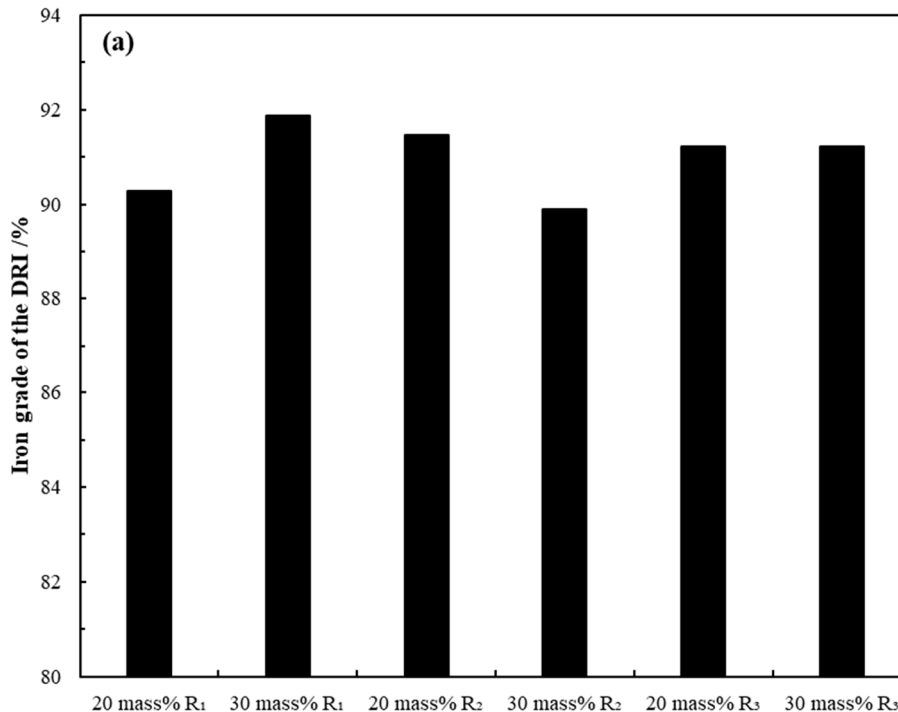


Figure 2. Cont.



Figure 2. Experimental results of R₁, R₂, R₃ and phosphorus removal of briquettes. (a) the function of R₁, R₂, R₃ on iron grade of DRI; (b) the function of R₁, R₂, R₃ on iron recovery and P-content of DRI.

3.2. XRD Analysis

To study the dephosphorization mechanism of this process, six briquettes with R₁, R₂, R₃ as reductant were analyzed by X-ray diffraction (10°–45°). The results are shown in Figure 3.

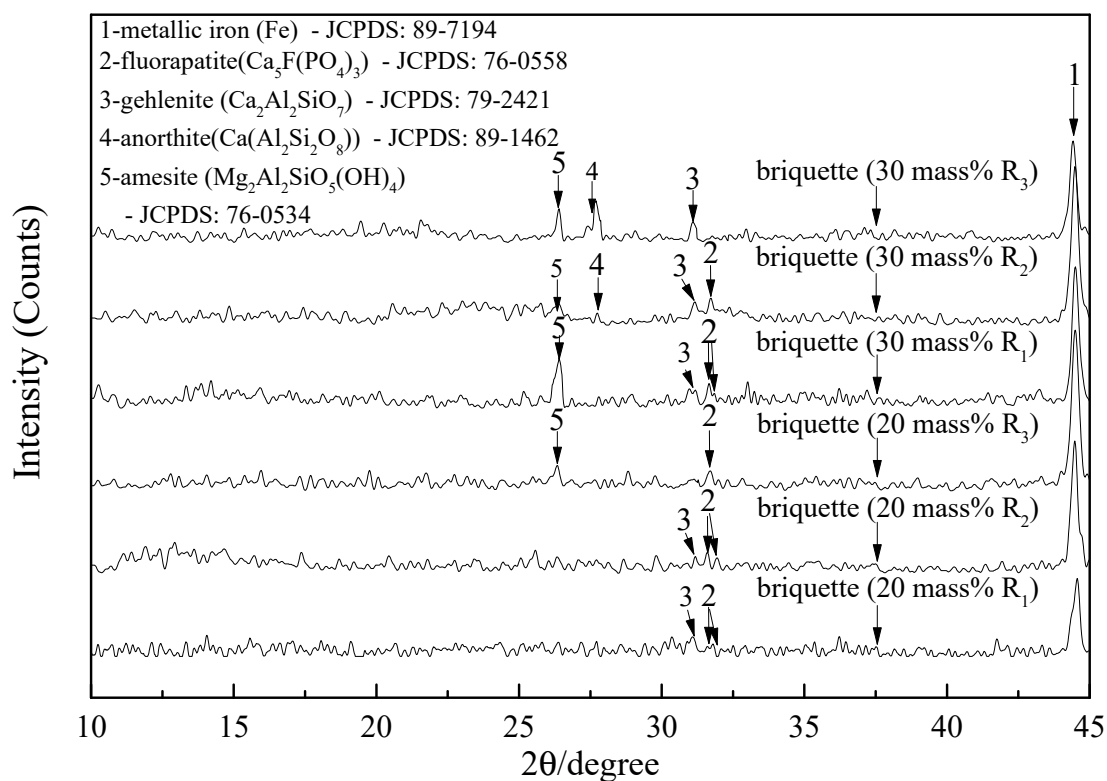
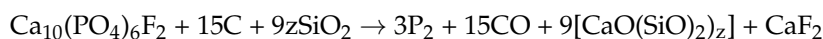


Figure 3. XRD analysis with JCPDS results of different briquettes.

As can be seen from Figure 3, hematite was reduced to metallic iron and the diffraction peak of fluorapatite showed different changes. Also, the diffraction peaks of gehlenite, anorthite, and amesite were observed in briquettes.

It is believed that silica plays an important role in promoting the reaction by providing a thermodynamic driving force and modifying the melting phenomena [23–25]. The chemical reaction of phosphate reduction can be summarized as follows:



Given that silica can promote the reduction of fluorapatite, some fluorapatites were reduced to P, and P melted into the metallic iron. The P in metallic iron was unable to be removed by physical separation which led to high P-content of DRI. This was consistent with the XRD analysis results of briquettes. The diffraction peaks of fluorapatite of briquettes obtained with 30 wt. % R_2 , R_3 as reductant were weaker than the diffraction peaks of fluorapatite of briquettes obtained with 20 wt. % R_2 , R_3 as reductant from the horizontal axis view. From the longitudinal axis view, the diffraction peaks of fluorapatite were higher in R_2 (low silica content as reductant) and were higher than compared to R_3 (high silica content as reductant). The effect of R_1 on the fluorapatite reduction was not only related to silica reduction effect, but also related to the reaction type of reduction [26] that is solid-solid reaction and gas-solid reaction. SEM-EDS analysis was thus used to investigate briquette microstructure to further reveal the effect of R_1 , R_2 , R_3 on the dephosphorization process.

3.3. Briquettes Microstructures

The phase translation and the morphological changes of iron-bearing minerals and fluorapatite at different roasting conditions were investigated. The results of SEM-EDS analysis of briquettes are shown in Figure 4.

Figure 4 illustrates that the generated iron particles gathered up and grew into a chain shape metallic iron. The different points represent the related area of a, b, c, d, e, and f, respectively. The related area had the same compositions. According to the result of point 1 analysis, when the R_1 was used as reductant, P-bearing minerals were mainly distributed in the gangue and in a small part of fluorapatite. Moreover, the result of point 2 analysis of the metallic iron illustrates that metallic iron did not contain phosphorus, which showed P-bearing minerals were not reduced to phosphorus element during the process with R_1 as reductant. The metallic iron in the briquettes aggregated significantly with a clear boundary to gangue mineral. From the view point of mineral processing, these metallic iron particles can be liberated from briquettes by grinding and magnetic separation to obtain a DRI with a low phosphorus content. Meanwhile, the result of point 3 analysis illustrates that metallic iron contained a high phosphorus content, where some fluorapatite were reduced to P and the P smelt into metallic iron. It is observed that the relationship of metallic iron and phosphorus is very intricate [27–29]. DRI contained high phosphorus content since the P in metallic iron cannot be removed by grinding magnetic separation. Those results were identical to the previous XRD analysis results. Therefore, coal slime can be used as reductant under certain conditions in the direct reduction process.

In addition, the analysis results of point 1 and point 5 of briquettes shows that gangue minerals contain Fe, which was weak-magnetic minerals and thus cannot be recovered by grinding and magnetic separation. That led to reduced Fe recovery rate in the magnetic separation process.

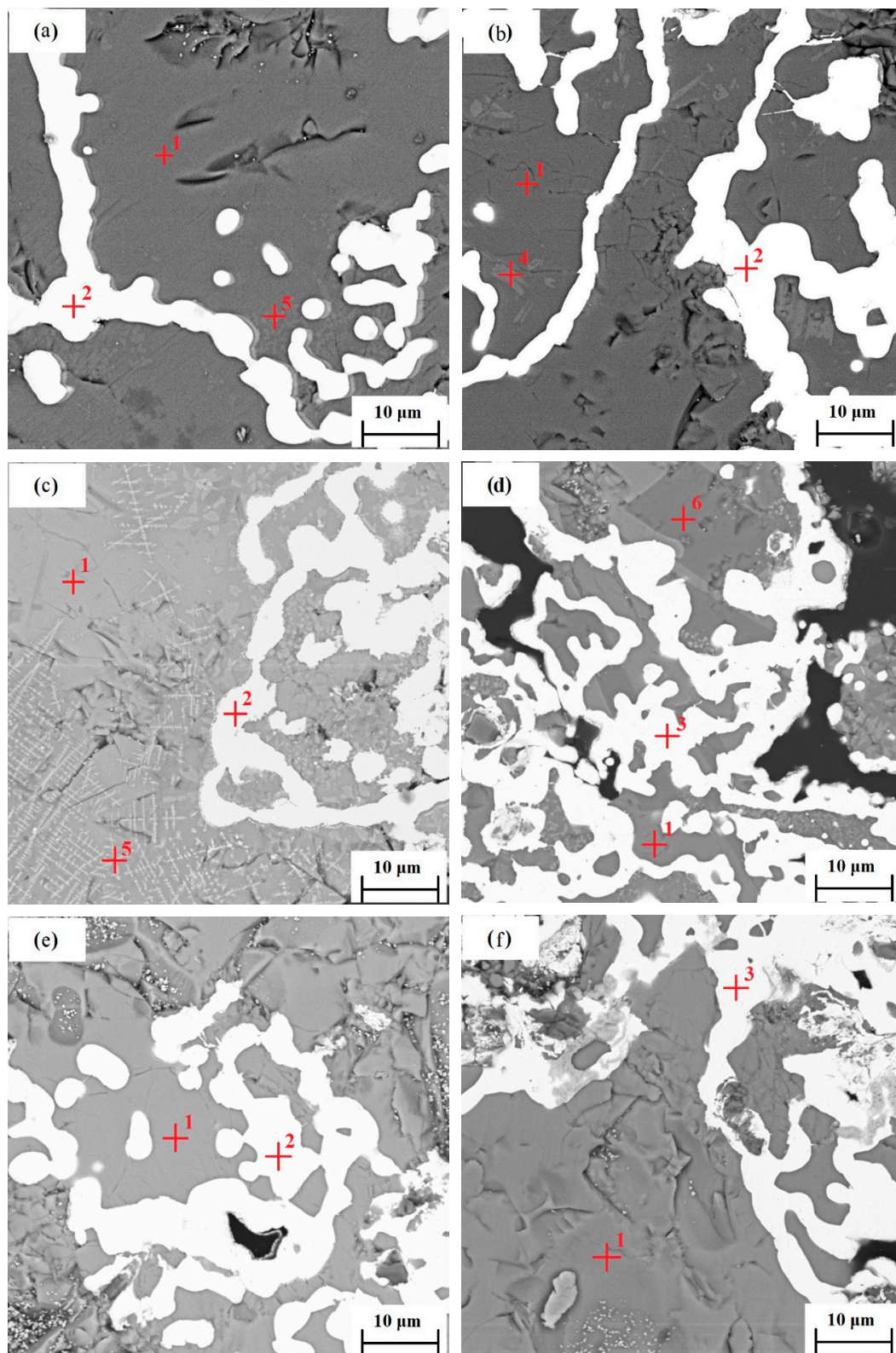


Figure 4. Cont.

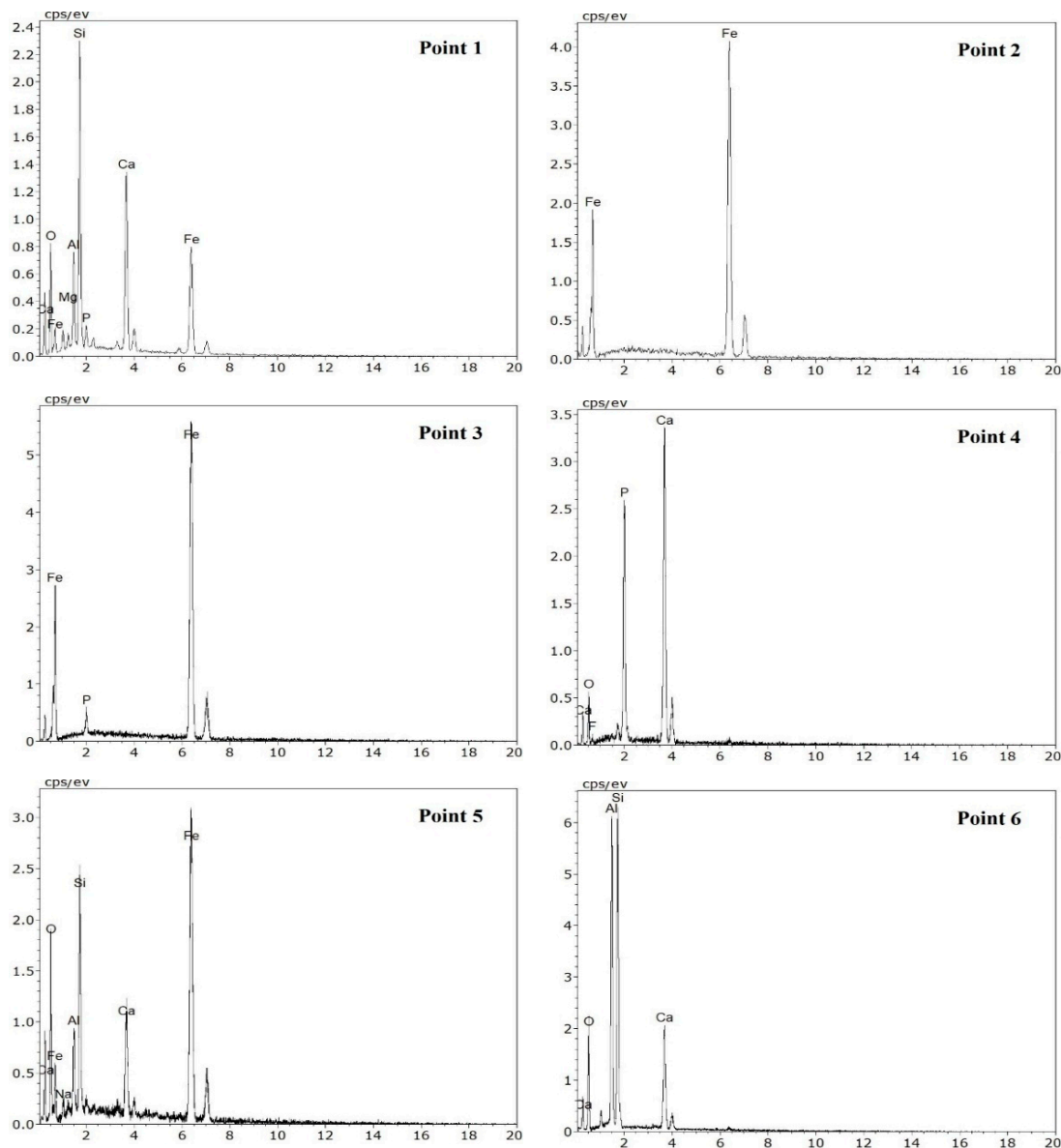


Figure 4. SEM-EDS analysis results of different briquettes. (a) 20 wt. % R_1 as reductant; (b) 30 wt. % R_1 as reductant; (c) 20 wt. % R_2 as reductant; (d) 20 wt. % R_2 as reductant; (e) 20 wt. % R_3 as reductant; (f) 30 wt. % R_3 as reductant. Point 1, 2, 3, 4, 5, and 6 were the results of point analysis in corresponding representative regions of Figure 4, respectively.

4. Conclusions

- (1) The process of the direct reduction followed by magnetic separation presents the ability of dephosphorization for treating high-phosphorus oolitic hematite. The blast furnace dust and coal slime can be used as reductant under certain conditions in this process.
- (2) Phosphorus is distributed in gangue mineral and fluorapatite in the direct reduction roasting process with blast furnace dust as reductant. P-bearing minerals are not reduced to phosphorus element, which was in favor of obtaining a DRI with low phosphorus content. A DRI of an iron grade of 91.88 wt. %, 88.38% $\varepsilon_{bfd(Fe)}$ and % P of 0.072 wt. % can be obtained with 30 wt. % blast furnace dust as reductant.
- (3) When the coal slime is used as reductant in the direct reduction roasting process, some fluorapatite is reduced to P and the P smelts into metallic iron. The phosphorus in metallic iron cannot be removed by physic separation, which led to DRI with high phosphorus content.

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