

Article

Process and Dephosphorization Mechanism for Producing Low-Phosphorus Steel via Direct Reduction–Electric Furnace Smelting Separation of Alkaline Briquettes from Refractory High-Phosphorus Oolitic Magnetite Concentrate

Mengjie Hu ^{1,2} , Deqing Zhu ^{1,2,*} , Jian Pan ^{1,2}  and Siwei Li ^{1,2,*}

- ¹ School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China; humengjie@csu.edu.cn (M.H.); pjcsu@csu.edu.cn (J.P.)
- ² Vale-CSU Joint Laboratory for Low-Carbon and Hydrogen Metallurgy, Central South University, Changsha 410083, China
- * Correspondence: dqzhu@csu.edu.cn (D.Z.); swli@csu.edu.cn (S.L.)

Abstract

High-phosphorus oolitic iron ores (HPOIOs) possess abundant reserves but are incompatible with conventional blast furnace ironmaking, as phosphorus migrates into hot metals during carbothermic reduction, preventing the production of low-phosphorus clean steel. To overcome this limitation, an innovative approach integrating alkaline briquette direct reduction and smelting separation was proposed. Briquettes were prepared from oolitic magnetite concentrate (52.01 wt% Fe, 0.29 wt% P, 0.11 wt% S) with a basicity (R) of 2.0 and 5 wt% MgO added as a desulfurizer. After direct reduction and smelting separation, the resulting metallic iron exhibited a content of 98.56 wt% Fe, with 0.036 wt% P and 0.046 wt% S, achieving an Fe recovery of 87.63%. The dephosphorization and desulfurization efficiencies reached 94.67% and 90.56%, respectively, meeting the clean steel requirements. Phosphorus was effectively stabilized within the gehlenite and merwinite phases as a solid solution of $\text{Ca}_3(\text{PO}_4)_2$, inhibiting its transfer to iron. Thermodynamic analyses confirmed that high basicity ($R \geq 2.0$) significantly suppressed P_2O_5 activity, preventing phosphate reduction. The formation of a $\text{Ca}_3(\text{PO}_4)_2$ – Ca_2SiO_4 solid solution further obstructed phosphorus migration. This dual mechanism of “chemical fixation and thermodynamic stabilization” enables efficient dephosphorization, offering a sustainable pathway for utilizing HPOIOs.

Keywords: high-phosphorus oolitic magnetite concentrate; direct reduction; smelting separation; low-phosphorus steel; dephosphorization



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1. Introduction

China, the world’s leading steel producer, manufactured approximately 1.05 billion tons of crude steel in 2024, reinforcing its pivotal role in global supply chains [1,2]. This production level, however, is accompanied by substantial environmental challenges, with the industry emitting approximately 180 million tons of CO_2 annually [3,4]. These emissions account for nearly one-fifth of the country’s industrial greenhouse gas output and contribute an estimated 15% to China’s total carbon footprint, highlighting the critical need for decarbonization strategies within the sector.

The environmental footprint of the steel industry originates predominantly from the blast furnace–basic oxygen furnace (BF–BOF) process, which employs coal and coke as both

fuel and reducing agents. This process inherently produces substantial volumes of CO/CO₂ emissions due to combustion and reduction reactions [5,6]. In China, carbon emissions associated with BF–BOF steelmaking in 2024 were reported to range from 1.8 to 2.5 metric tons per ton of crude steel, with the blast furnace unit alone contributing approximately 1.5 tons—accounting for 70% to 90% of the total CO₂ emissions within integrated steel plants [7,8]. Given its high carbon intensity, this conventional method is increasingly viewed as a critical obstacle to worldwide decarbonization efforts and sustainable industrial development. In light of these challenges, the China Iron and Steel Association (CISA) has introduced stringent energy conservation and coal consumption reduction policies to facilitate a transition toward greener steel production.

Electric smelting furnace (ESF) technology has emerged as a transformative alternative by shifting from coal to direct reduced iron (DRI) or scrap metal as the primary feedstock. Data from the Steel Manufacturers Association (SMA) indicate that the ESF process emits only 0.3 tons of CO₂ per ton of steel—a reduction of 75% compared with the 1.6 tons emitted via the conventional BF–BOF route [9]. This positions ESF as an environmentally sustainable solution that supports resource circularity and reduced energy consumption, essential for industrial decarbonization. Several demonstration projects, including million-ton-scale DRI–ESF plants launched by the Baowu Group in Zhanjiang and the HBIS Group in Xuanhua, provide valuable references for low-carbon steelmaking in China [10–12].

A further significant challenge lies in China's considerable external dependency on iron ore imports. In 2024, the country's iron ore imports reached 1.237 billion tons, with more than 80% of this volume supplied by the four leading global mining corporations: Vale, BHP, Fortescue Metals Group (FMG), and Rio Tinto [13,14]. This heavy reliance poses substantial risks to the stability and security of the strategic resource supply chain. Consequently, enhanced utilization of domestic iron ore resources is considered essential for strengthening supply chain resilience and ensuring long-term sustainability. Estimates from the U.S. Geological Survey indicate that China holds more than 80 billion tons of iron ore reserves, comprising over 7 billion tons of high-phosphorus oolitic iron ore (HPOIO), a category of ore with worldwide reserves estimated to exceed 200 billion tons [15]. Despite its abundance, the industrial processing of HPOIO remains challenging owing to its elevated phosphorus content (ranging from 0.1% to 1.5%), complex mineralogical composition, and finely disseminated texture, all of which have thus far limited its large-scale exploitation.

In conventional blast furnace ironmaking, phosphorus-bearing minerals undergo reactions with metallic iron under carbothermic reduction conditions, resulting in the formation of iron phosphides. These compounds impair the crystalline integrity of steel, leading to degraded weldability, inferior thermomechanical properties, and reduced low-temperature toughness while also increasing the propensity for cold brittleness [16–18]. In accordance with the Chinese national standard GB/T 699-2015 [19], the phosphorus content in high-quality structural steel is strictly limited to a maximum of 0.035%. This specification underscores the necessity for efficient dephosphorization either prior to or during the smelting process.

Research efforts have been devoted to developing processing strategies for HPOIO. These methods span several technological areas, including conventional mineral beneficiation, hydrometallurgical extraction, and thermal reduction techniques such as magnetization roasting (MR–MS) and direct reduction (DR–MS), both of which are integrated with magnetic separation [20–22]. These techniques, however, are subject to considerable limitations: the ultrafine intergrowth of minerals complicates liberation and separation; hydrometallurgical approaches require large quantities of acidic reagents and generate hazardous waste [23–26]; MR–MS improves processability without substantially reducing

phosphorus content; and DR–MS demands temperatures exceeding 1200 °C with high reductant consumption, resulting in elevated energy use and carbon emissions.

Although hot metal pretreatment dephosphorization and basic oxygen furnace (BOF) refining have been extensively investigated, these end-of-pipe methods are incompatible with HPOIO due to stringent requirements for initial phosphorus levels ($\leq 0.2\%$ in hot metals) along with high operational complexity and cost [27–31]. Moreover, conventional dephosphorization depends on simultaneously optimizing three thermodynamically conflicting parameters, namely, low temperature, an oxidizing atmosphere, and high slag basicity, to facilitate the oxidation of [P] to P_2O_5 and subsequent stabilization in slag as $Ca_3(PO_4)_2$ —conditions unattainable in conventional BF reduction environments.

Despite considerable experimental studies on this ore have demonstrated satisfactory performance in iron recovery and dephosphorization, critical challenges remain in existing approaches [32,33]. For instance, hydrometallurgical leaching processes suffer from high acid consumption and difficult disposal of waste acid, while pyrometallurgical routes require large quantities of dephosphorization agents and often result in incomplete phosphorus removal. These limitations severely compromise the quality of the final product. Therefore, it is imperative to develop more efficient and sustainable processing strategies for treating refractory high-phosphorus oolitic iron ore. An innovative process integrating direct reduction of alkaline briquettes with electric furnace smelting was developed for treating oolitic magnetite concentrate (OMC), a preupgraded concentrate derived from HPOIO [27]. The process involves cold-bonded briquetting of OMC with alkaline fluxes, eliminating the need for energy-intensive sintering or pelletization. Subsequent solid-state direct reduction at moderate temperatures facilitates the selective reduction of iron oxides, whereas alkaline additives suppress phosphorus migration into metallic iron. Smelting separation of the reduced briquettes produces a metal phase meeting standard clean steel specifications ($P \leq 0.04\%$) and a phosphorus-enriched slag phase (P recovery $> 94\%$). This method combines phosphorus fixation during reduction with efficient iron–slag separation, circumventing the complexities and costs associated with downstream dephosphorization.

A comprehensive investigation has been conducted into the reduction behavior, slag–metal partitioning efficiency, and underlying thermodynamics of dephosphorization. This work establishes a short, integrated metallurgical route from refractory high-phosphorus iron ore to clean steel, providing a sustainable and strategically viable pathway for the utilization of challenging domestic iron ore resources.

2. Experimental Section

2.1. Material Characteristics

The two ores utilized in the present research were chemically characterized, and their detailed compositions are quantified in Table 1. Chemical analysis revealed that HPOIO has a total iron (TFe) grade of 35.05%, which is typically inadequate for direct application in conventional iron and steel production. Accordingly, in prior research, HPOIO underwent a preconcentration process consisting of magnetizing roasting and subsequent magnetic separation. This treatment yielded a concentrated product, designated OMC, with a significantly elevated TFe content of 52.06% [27,28]. Despite this, the OMC was found to contain elevated levels of deleterious impurities, specifically Al_2O_3 , SiO_2 , and P. In particular, the phosphorus content was 0.30%. In traditional blast furnace ironmaking, phosphorus is predominantly reduced and dissolved into the molten iron, with no efficient route for its removal, thereby rendering the production of low-phosphorus steel from such high-phosphorus feed materials unfeasible. Thus, it is essential to develop alternative ironmaking technologies that can effectively process this category of refractory iron ore.

Table 1. Chemical analysis of ores (wt%).

Types	TFe	K ₂ O	CaO	Na ₂ O	Al ₂ O ₃	FeO	SiO ₂	MgO	P	S
HPOIO	35.05	0.68	1.36	0.045	9.87	20.01	25.56	1.21	0.45	0.38
OMC	52.07	0.13	0.28	0.019	9.31	25.49	15.93	1.06	0.30	0.09

Note: Total iron (TFe) and ferrous oxide (FeO) were determined by chemical titration, while the remaining elements were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

As evidenced by the mineralogical characterization presented in Figure 1, and Table 2 presents the spectral data obtained from the EDS point scans shown in Figure 1. The OMC is primarily composed of magnetite, hematite, amorphous aluminosilicates, quartz, and fluorapatite. Crucially, the microstructure exhibits a complex concentric ring pattern in which ultrafine-grained magnetite is intimately intergrown with aluminosilicate phases, quartz, and fluorapatite [28]. This interlocking texture encapsulates iron minerals within a gangue matrix, significantly hindering the liberation of magnetite through physical beneficiation methods. Furthermore, extensive substitution of Al³⁺ into the crystal lattice of iron oxides presents an additional barrier to efficient iron–aluminum separation via conventional physiochemical processing routes. These inherent mineralogical constraints—namely, ultrafine intergrowth and isomorphous substitution—impose substantial challenges for the utilization of this refractory iron ore resource.

Table 2. SEM–EDS analysis.

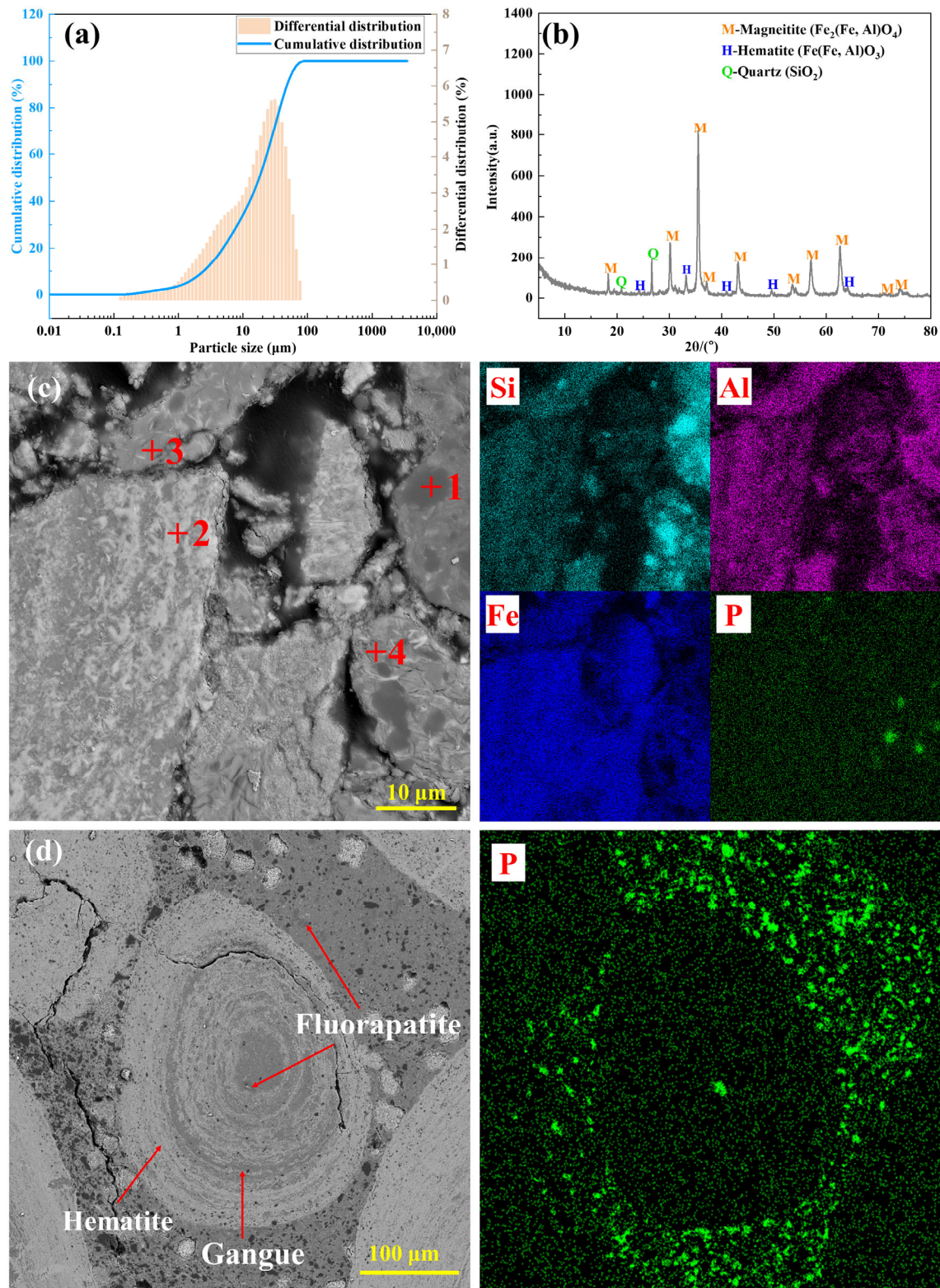
Point	At %								Mineral Phase
	Fe	P	Mg	Si	Al	F	Ca	O	
1	—	—	—	65.21	—	—	—	34.79	SiO ₂
2	52.51	—	—	3.04	3.41	—	—	41.02	(Fe, Al) ₃ O ₄
3	26.52	—	2.00	14.38	15.43	—	—	41.67	4FeO·Al ₂ O ₃ ·3SiO ₂
4	—	15.96	—	—	—	3.45	28.42	50.45	Ca ₅ (PO ₄) ₃ F

In this study, pulverized coal served as the reductant. The industrial analysis results (Table 3) indicate that the coal sample consisted of 50.32% fixed carbon (FC_{ad}), 10.13% ash (A_{ad}), and 39.55% volatile matter (V_{ad}).

Table 3. Industrial analysis of coal (wt%).

Components	FC _{ad}	A _{ad}	V _{ad}
Coal	50.32	10.13	39.55

The alkaline additives employed in this study, including CaCO₃ and MgO, were analytical-grade (AR) reagents sourced from the Chemical Platform of Central South University, with chemical purities meeting experimental specifications.



The labels +1, +2, +3, and +4 correspond to the locations of EDS point analysis.

Figure 1. Ore characteristics. (a–c) OMC; (d) HPOIO.

2.2. Experimental Procedure

A schematic flowchart of the integrated process is presented in Figure 2. The procedure combines direct reduction of basic briquettes with subsequent smelting separation in an electric furnace and consists of three main stages: preparation of basic briquettes, coal-

based direct reduction, and smelting separation. In the briquette preparation stage, raw ore powder and CaCO_3 were thoroughly homogenized. The powder mixture was then compacted into cylindrical briquettes (11 mm in diameter $\times$ 16 mm in length) using a JYP-15-3 hydraulic press (Jiaxin Hai, Tianjin, China) under 3-ton pressure with a dwell time of 30 s. In the reduction stage, the prepared briquettes were uniformly mixed with pulverized coal and charged into sealed corundum crucibles. Isothermal reduction was conducted in a JC2-12-10A muffle furnace (Jingcheng Instruments, Qingdao, China) at 1050 °C for 120 min with a C/Fe mass ratio of 2 [28,30]. After reduction, the crucibles were immediately extracted and covered with additional coal to minimize reoxidation during natural cooling to ambient temperature. During the smelting separation stage, the reduced briquettes were placed in a magnesia crucible, which was then positioned in a VSF resistance furnace (Boyuntong Instruments, Nanjing, China) and maintained at 1550 °C for 20 min. The entire melting process was performed under a continuous argon flow of 2 L/min to prevent oxidation. Upon completion, the crucibles were withdrawn from the furnace and cooled to room temperature under the same argon atmosphere. The solidified products were subsequently manually crushed to separate the metallic and slag phases. Moreover, to guarantee the reliability and reproducibility of the findings, all experiments involving reduction and smelting separation were performed a minimum of three times, with the results presented as averages.

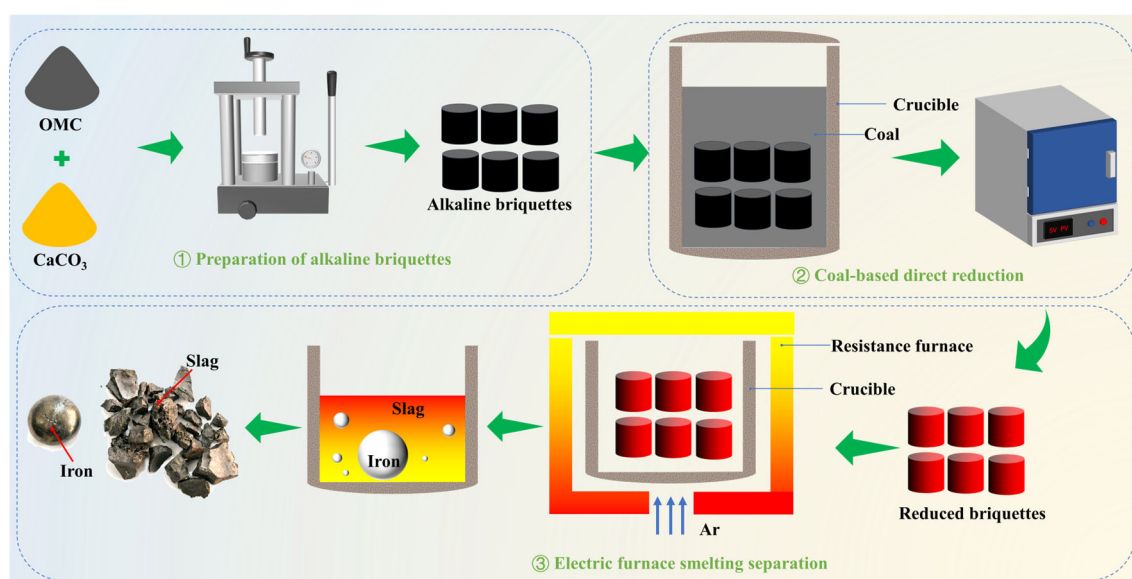


Figure 2. Flowsheet for the treatment of alkaline briquettes via direct reduction coupled with electric furnace smelting separation.

The metallization degree and basicity of the reduced samples were evaluated via Equation (1) and Equation (2), respectively. Furthermore, the iron recovery efficiency in the metallic phase and the dephosphorization rate were assessed via Equations (3) and (4), respectively.

$$\mu = \frac{K_{Fe}}{N_{Fe}} \times 100\% \quad (1)$$

In Equation (1), the symbol μ signifies the degree of metallization. The terms K_{Fe} and N_{Fe} designate the contents of metallic iron and total iron (in mass percent) in the reduced briquettes, respectively.

$$R = \frac{w_{CaO}}{w_{SiO_2}} \times 100\% \quad (2)$$

where w_{CaO} and w_{SiO_2} denote the mass fractions of CaO and SiO₂ in the sample, respectively.

$$\varphi = \frac{n \times w}{N \times F} \times 100\% \quad (3)$$

$$\omega = \left(1 - \frac{n \times q}{N \times S}\right) \times 100\% \quad (4)$$

In these formulations, φ represents the iron recovery efficiency (%), where n designates the mass of metallic iron recovered after smelting (g), and w corresponds to the iron content in the metallic product (%). The symbol N denotes the initial mass of the reduced briquettes charged (g), whereas F indicates the total iron grade of the feed material (%). Moreover, ω refers to the dephosphorization rate (%), with q representing the phosphorus content in the metallic phase (%), and S designates the P content in the feed prior to smelting (%).

In parallel, thermodynamic simulations were conducted using the FactSage8.1 software package, employing both the pure substance and oxide databases to calculate the equilibrium phase relationships within the slag system. These calculations provide a theoretical representation of the material equilibrium states under idealized conditions.

3. Results and Discussion

3.1. Effects of Basicity on the Direct Reduction and Melting Separation Processes

In accordance with previous experimental studies [26,27], the optimal conditions for the coal-based direct reduction of cold-bonded briquettes under natural basicity were a roasting temperature of 1050 °C for 2 h and a C/Fe mass ratio of 2. These conditions were subsequently maintained to methodically examine the effect of basicity. The influence of basicity on the extent of metallization achieved during the coal-based reduction process is presented in Figure 3. As the basicity increased from its natural level ($R = 0.035$) to 1.0, the metallization rate notably increased from 76.75% to 84.41%. Beyond this point, a further increase in basicity up to $R = 2.5$ resulted in a stabilization of the metallization degree, indicating a plateau in the enhancement effect. These findings suggest that moderately increasing the basicity effectively promotes the reduction efficiency of the briquettes, whereas excessive basicity does not yield additional benefits under the given conditions.

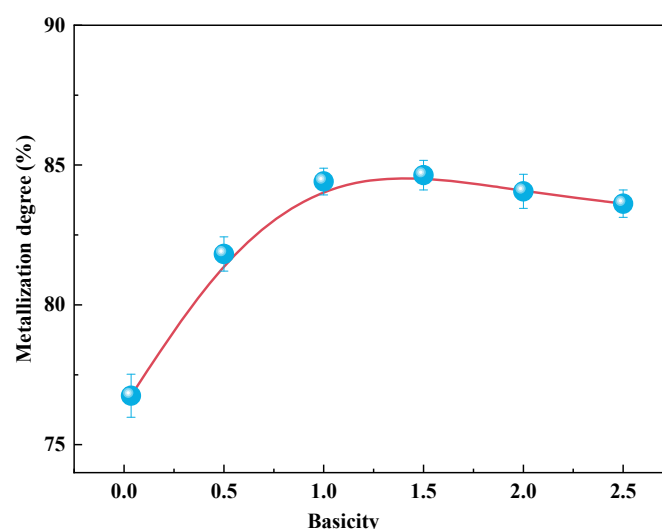


Figure 3. Effect of basicity on the metallization degree of reduced samples.

Figure 4 shows the macroscopic morphology of slag–iron separation after electric furnace smelting under different basicity conditions. The results show that effective separation between slag and iron was attained as the basicity increased from 0.035 to 2.0. However,

at a basicity of 2.5, metallic inclusions were observed within the slag phase, suggesting a decrease in separation efficiency under higher alkaline conditions. Mechanistic analysis indicates that excessive basicity increases the slag viscosity and increases the melting temperature, significantly deteriorating the melt fluidity and thereby impeding the kinetic process of slag–metal interface separation [34,35].



Figure 4. Macroscopic morphology of slag and iron separation after smelting under different basicity conditions. (a) $R = 0.035$; (b) $R = 0.5$; (c) $R = 1.0$; (d) $R = 1.5$; (e) $R = 2.0$; (f) $R = 2.5$.

The influence of R on the partitioning behavior of iron and phosphorus within the molten iron phase is illustrated in Figure 5. Over the basicity range of $R = 0.035$ – 2.5 , the purity of the iron remained consistently high, stabilizing between 98% and 99%. In contrast, the iron recovery decreased modestly from 91% to 88% with increasing basicity (Figure 5a).

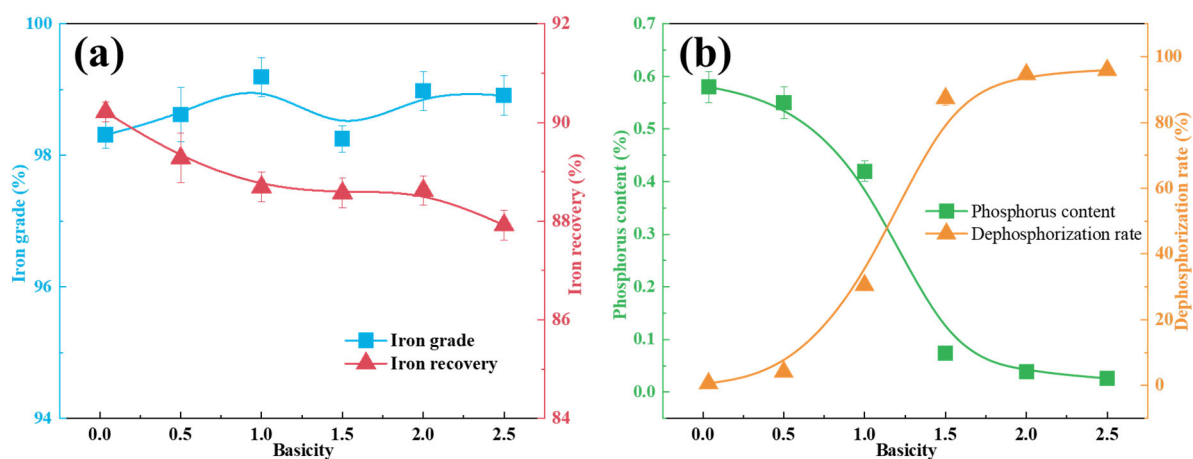


Figure 5. Influence of basicity on the key constituents of the iron phase after smelting. (a) Iron content index; (b) phosphorus content index.

In contrast, phosphorus partitioning exhibited a strong correlation with basicity (Figure 5b). As R increased from 0.035 to 2.0, the P content in the metallic phase significantly reduced from 0.58% to 0.039%, accompanied by a marked improvement in the dephosphorization efficiency from 0.63% to 94.56%. A further increase in basicity to $R = 2.5$ resulted in an additional reduction in the phosphorus content to 0.026%, with the dephosphorization rate reaching 95.85%. These results indicate that maintaining the basicity at $R = 2$ offers an optimal compromise between efficient phosphorus removal and process economics.

3.2. Effect of MgO Application on Direct Reduction and Subsequent Smelting Separation

In the OMC system, sulfur (S) with an initial content of 0.11% requires co-removal alongside phosphorus because of its detrimental induction of hot-working embrittlement, which significantly compromises steel performance. The experimental results demonstrate that at $R = 2$, the S content in molten iron decreases to 0.09% but still exceeds the conventional steel sulfur threshold of 0.055%. This reveals unresolved optimization potential in the thermodynamic equilibrium control of sulfur within the current process, necessitating enhancements in the sulfur partition coefficients or improvements in the kinetic conditions to achieve deep desulfurization.

Industrial hot metal desulfurization technologies primarily employ two reaction systems: calcium-based agents (CaO , CaC_2) and magnesium-based agents (MgO and its derivatives). Compared with that of Ca^{2+} , the ionic radius of Mg^{2+} is smaller than that of Ca^{2+} , suggesting that MgO has superior sulfur affinity and diffusion kinetics because of its higher charge density, which endows magnesium-based systems with advantages in terms of both the sulfur capacity and desulfurization rate [33]. Building on this foundation, our study innovatively introduces MgO additives to construct a CaO – MgO alkaline slag system, systematically investigating its synergistic regulatory mechanism on the slag–metal interface behavior and migration patterns of impurity elements (P/S) in the iron phase during melting separation.

Figure 6 shows the macroscopic morphology of slag–iron separation after electric furnace smelting under different MgO dosage. Effective slag–iron separation was achieved in both phases as the MgO dosage increased from 0% to 10%. However, at 15% MgO , incomplete separation occurred, with iron particles failing to coalesce and metallic iron entrapped in the slag phase. Mechanistic studies revealed that elevated MgO levels facilitate the formation of refractory silicate phases—including monticellite (CaMgSiO_4) and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$)—which markedly increase slag viscosity, compromise melt fluidity, and ultimately retard the kinetics of slag–metal separation.



Figure 6. Macroscopic morphology of slag and iron separation after smelting under different MgO dosage. (a) 0%; (b) 5%; (c) 10%; (d) 15%.

As illustrated in Figure 7, the addition of MgO selectively regulates the separation behavior of Fe, P, and S within the metallic iron phase during smelting. With increasing MgO dosage, the iron grade in the metallic phase gradually decreased from 98.98% to 97.85%, accompanied by a decrease in iron recovery from 88.62% to 85.87% (Figure 7a). These results suggest that excessive MgO addition impairs the enrichment efficiency of iron.

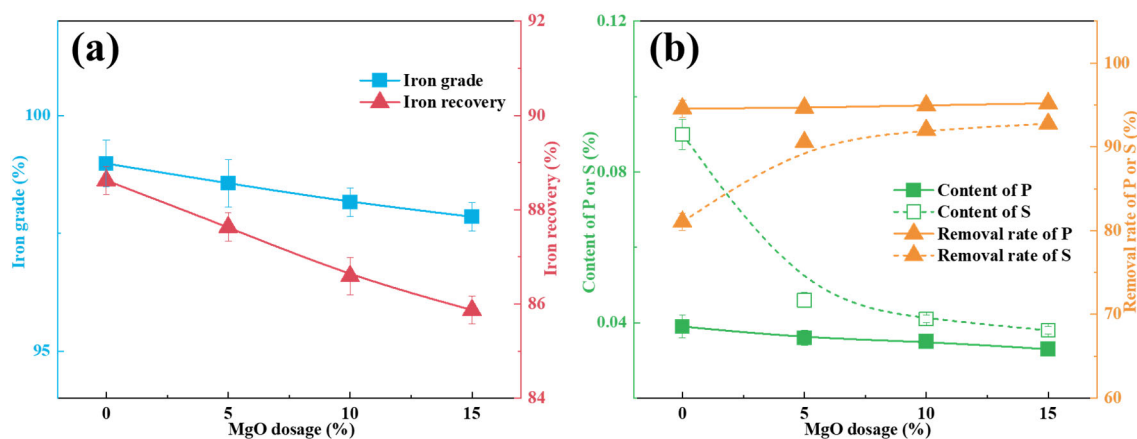


Figure 7. Effect of the MgO dosage on the composition of the metallic phase following the smelting process. (a) Iron content index; (b) phosphorus content index.

Divergent removal behaviors were observed for P and S, as depicted in Figure 7b. As the MgO dosage increased from 0% to 5%, the sulfur content markedly decreased from 0.09% to 0.046%. In contrast, the phosphorus content only marginally decreased from 0.039% to 0.036%. A further increase in MgO addition to 15% led to a gradual decline in the contents of both elements, reaching 0.038% S and 0.033% P. These results demonstrate the specific removal effect of MgO on sulfur compared with its weaker influence on phosphorus migration. A comprehensive evaluation indicates that the addition of 5% MgO achieves an optimal balance between the slag–metal separation efficiency and impurity removal effectiveness.

As shown in Table 4, the optimized process consistently controls phosphorus and sulfur contents in the metallic phase at 0.036% and 0.046%, respectively, meeting the composition standards for common steel grades ($P \leq 0.045\%$, $S \leq 0.055\%$). Concurrently, the slag phase shows significant phosphorus enrichment to 0.528%, confirming effective phosphorus partitioning into the slag. This short-process metallurgical route successfully enables the targeted conversion of HPOIO into low-phosphorus clean steel through coordinated pre-reduction and smelting separation.

Table 4. Key chemical constituents of the metallic iron phase following smelting (wt%).

Composition	TFe	Al ₂ O ₃	MgO	Na ₂ O	SiO ₂	CaO	K ₂ O	S	P
Metallic iron phase	98.56	0.045	0.017	0.0068	0.12	0.026	0.004	0.046	0.036
Slag phase	10.04	30.82	2.189	0.0021	17.42	35.83	0.228	0.062	0.528

4. Characterization of Melting Slags

This study employed XRD phase analysis, XPS chemical state characterization, and EPMA microregional composition mapping to systematically investigate the mineral evolution and interface enrichment mechanisms of phosphorus in smelting slags with various basicity levels ($R = 0.035$ – 2.5).

4.1. XRD

As shown in Figure 8, the XRD patterns of slags with varying basicities reveal distinct phase evolution characteristics. At natural basicity ($R = 0.035$), a broad hump in the 20 – 40° range (indicative of the amorphous glass phase) coexists with metallic iron diffraction peaks, suggesting the presence of minor incompletely separated iron particles in the slag phase. When R increases to 0.5 – 1.0 , only amorphous scattering patterns are observed,

confirming the complete vitrification of the slag phase. Notably, crystallization occurs when $R \geq 1.5$: Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), ferro-magnesian spinel ($(\text{Fe,Mg})\text{Al}_2\text{O}_4$), and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$) form at $R = 1.5$, whereas wüstite (FeO) precipitates at $R = 2.0$ – 2.5 . This phase evolution demonstrates that higher basicity ($R \geq 1.5$) significantly increases the slag liquidus temperature, promoting directional crystallization of thermally stable minerals.

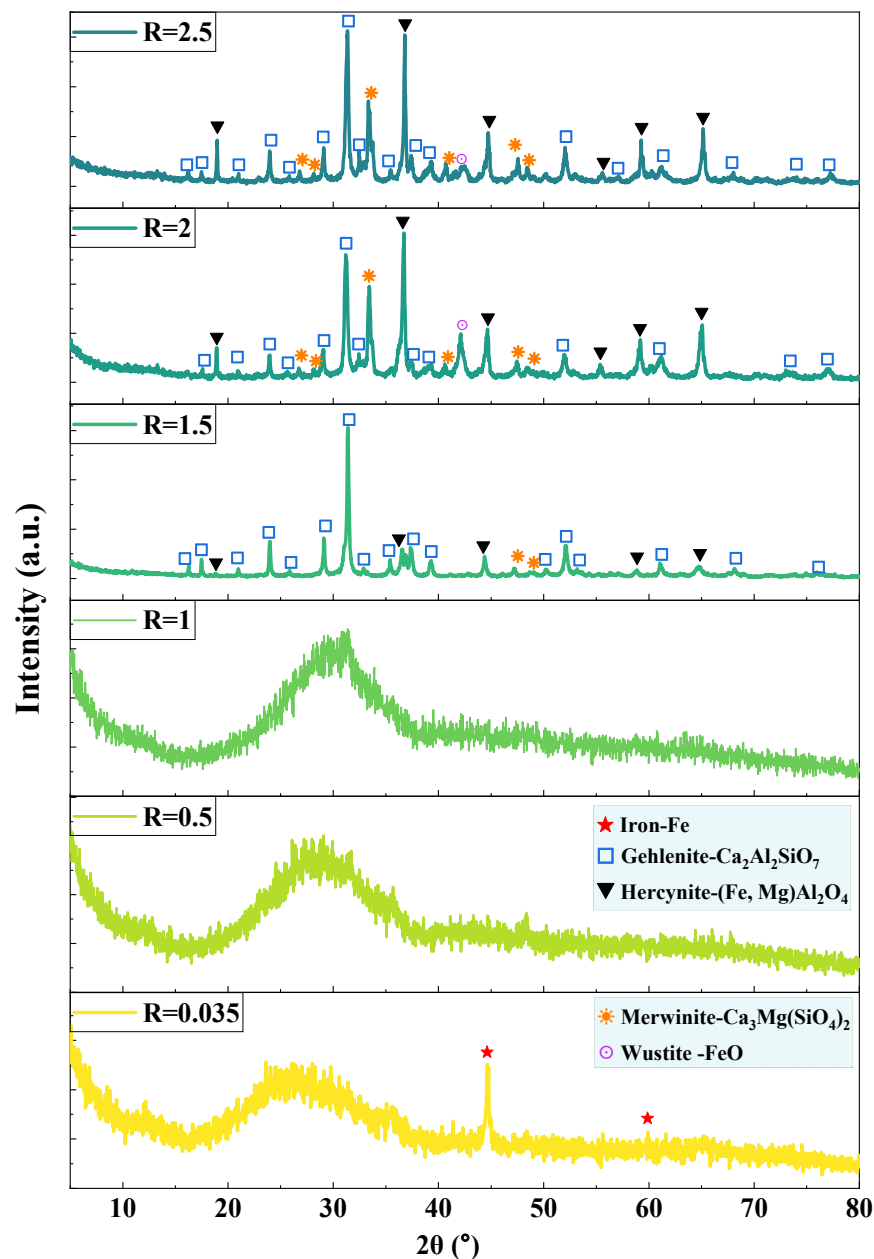


Figure 8. XRD patterns of the slag samples.

4.2. XPS

As shown in Figure 9, XPS analysis was employed to systematically investigate the speciation transformation of phosphorus within the slag phase. The survey spectrum (Figure 9a) along with the high-resolution P 2p spectra (Figure 9b) revealed that phosphorus enrichment in the slag notably intensified as the basicity increased from 0.035 to 2.5. The characteristic P 2p peak exhibited a positive binding energy shift from 133.12 eV to 133.43 eV ($\Delta = 0.31$ eV), indicating enhanced stability of the chemical environment in the $\text{Ca}_3(\text{PO}_4)_2$ crystal structure under high basicity conditions, which facilitates effective phosphorus immobilization in cal-

cium phosphate phases. Quantitative photoelectron intensity analysis (Figure 9c) revealed exponential growth of the phosphorus signal from 26.83 cps·eV to 6335.18 cps·eV as R increased from 0.035 to 2.0, followed by a decrease in the growth rate (6464.28 cps·eV at R = 2.5), corresponding to an increase in the phosphorus accommodation capacity. These series of characterization data collectively demonstrate the positive correlation between basicity and phosphorus enrichment behavior in the slag system.

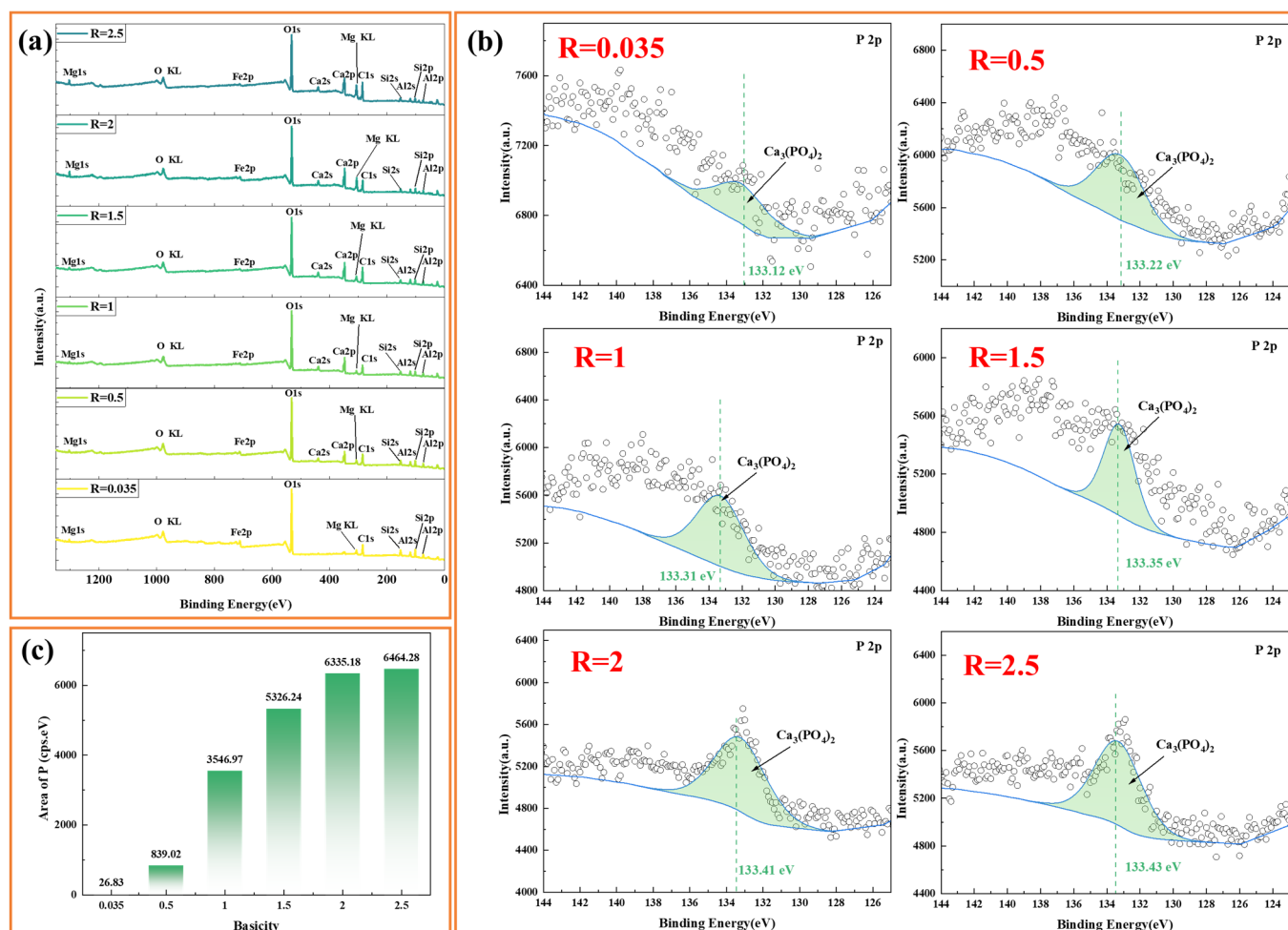


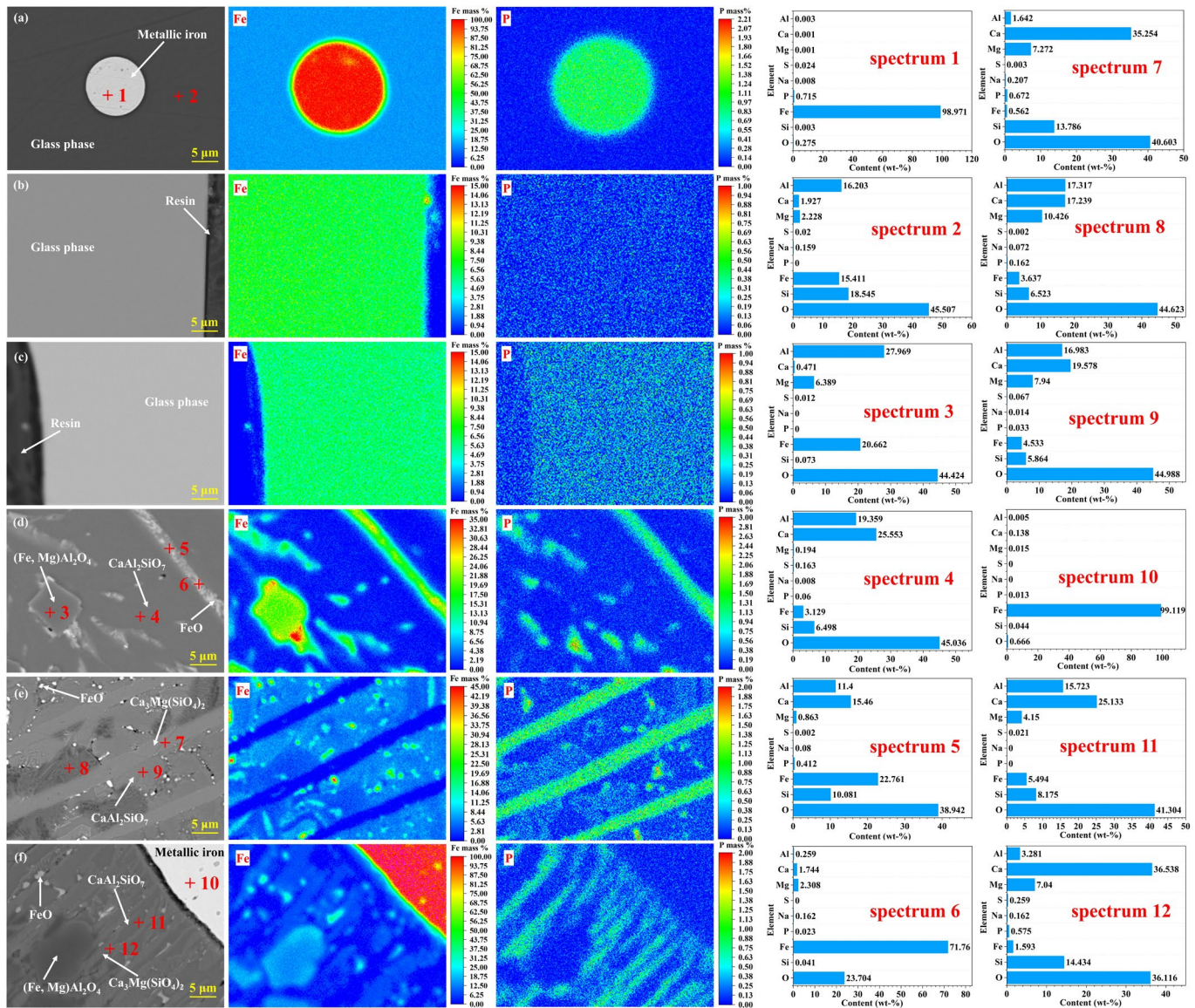
Figure 9. XPS patterns of the slag samples. (a) XPS survey; (b) 2p fine spectrum of P; (c) area of P.

4.3. EPMA

As shown in Figure 10, EPMA microregional analysis of slag melts with varying basicity levels revealed the phase distribution patterns of phosphorus. Under natural basic conditions ($R = 0.035$), the slag matrix primarily consisted of an amorphous glass phase (phosphorus was undetectable), whereas the residual metallic iron phase presented a phosphorus content of 0.715% (Figure 10a), demonstrating the inability of low-basicity systems to achieve phosphorus fixation in the slag phase. When R increased to 0.5 and 1.0, phosphorus displayed a homogeneous distribution within the glass phase, with progressively increasing concentration gradients correlated with increasing basicity (Figure 10b,c), confirming the onset of phosphorus migration toward the slag phase.

Crystalline-dominated regions ($R \geq 1.5$) exhibited distinct phase-controlled phosphorus enrichment behaviors. At $R = 1.5$, phosphorus preferentially resided in elongated $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{-FeO-Ca}_3(\text{PO}_4)_2$ composite solid solutions (0.412%, Figure 10d). Increasing the basicity to $R = 2.0$ induced phosphorus migration into multiphase $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2\text{-FeO-Ca}_3(\text{PO}_4)_2$ solid solutions (0.672%, Figure 10e). At $R = 2.5$, phosphorus further accumulated

in elongated $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - FeO - $\text{Ca}_3(\text{PO}_4)_2$ solid solutions (0.575%, Figure 10f), with residual iron-phase phosphorus sharply reduced to 0.013%. This evolution pattern confirms that the alkaline briquette prereduction-smelting process involves calcium silicate-mediated lattice entrapment mechanisms (via $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$), effectively inhibiting both $\text{Ca}_3(\text{PO}_4)_2$ thermal decomposition and phosphorus diffusion toward metallic phases, thereby providing microstructural evidence for basicity-driven phosphorus removal strategies.



The labels +1 to +12 correspond to the locations of EPMA point analysis.

Figure 10. EPMA of slag samples with different basicities. (a) $R = 0.035$; (b) $R = 0.5$; (c) $R = 1.0$; (d) $R = 1.5$; (e) $R = 2$; (f) $R = 2.5$.

5. Mechanism of Dephosphorization

5.1. Thermal Stability of $\text{Ca}_3(\text{PO}_4)_2$

Extensive studies have demonstrated that the reduction and migration of phosphorus minerals are governed by the activity of P_2O_5 components within the system [26,27]. The fundamental approach to suppressing these processes lies in reducing P_2O_5 activity. Thermodynamic calculations comparing the P_2O_5 activity of pure $\text{Ca}_3(\text{PO}_4)_2$ and HPOIO

under varying basicity conditions (Figure 11) provide critical insights into the feasibility of the phosphorus reaction. Notably, in comparison to the pure $\text{Ca}_3(\text{PO}_4)_2$ system, the HPOIO sample demonstrates a sharp exponential enhancement in P_2O_5 activity under isothermal conditions. This significant enhancement can be largely attributed to the existence of SiO_2 and Al_2O_3 in the ore matrix, which considerably lower the activation energy necessary for the generation of volatile P_2O_5 .

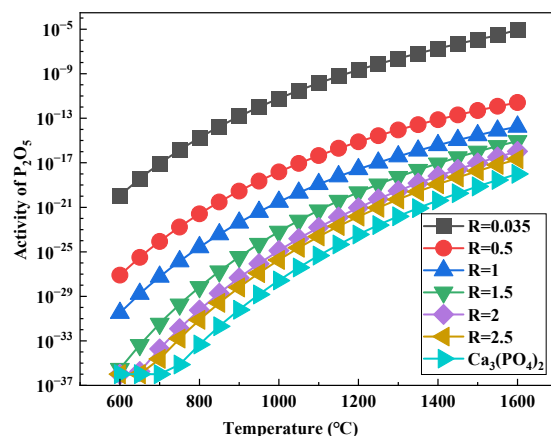


Figure 11. Activity of P_2O_5 components in different systems.

Importantly, the increase in basicity from 0.035 to 2.5 induces a substantial reduction in P_2O_5 activity within the iron ore system, demonstrating the enhanced thermodynamic stability of $\text{Ca}_3(\text{PO}_4)_2$ under high-basicity conditions, which effectively suppresses the liberation of reactive P_2O_5 . Furthermore, regardless of the system configuration, P_2O_5 activity increases exponentially with increasing temperature, confirming that low-temperature operation serves as another critical factor for controlling phosphorus mineral decomposition. The elucidated thermodynamic stabilization mechanism of P_2O_5 provides guiding significance for industrial electric furnace smelting. To effectively remove phosphorus, the process must be conducted within an operational window of lower temperature and higher slag basicity, thereby promoting the stable fixation of phosphorus within the slag phase.

5.2. Slag Phase Mechanism

Figure 12 presents the high-temperature characteristics of the slag phase. As shown in Figure 12a, with increasing basicity from $R = 0.035$ to 1.0, the primary crystalline phase transitioned from mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), accompanied by a reduction in the liquidus temperature from above 1600°C to approximately 1350°C . At $R = 1.5$, the phase assemblage transitioned to gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), accompanied by a rebound in the liquidus temperature to approximately 1500°C . With a further increase in basicity to $R = 2.0$ – 2.5 , the system migrated into regions dominated by dicalcium silicate (Ca_2SiO_4), resulting in liquidus temperatures exceeding 1600°C . Notably, the $\text{Ca}_3(\text{PO}_4)_2$ solid solution identified within dicalcium silicate phases under high-basicity conditions ($R \geq 2.0$) presented characteristics consistent with the phosphorus speciation profiles obtained via EPMA. This correlation confirms that phosphorus attains thermal stability via the formation of a $\text{Ca}_3(\text{PO}_4)_2$ – Ca_2SiO_4 solid solution, thereby effectively inhibiting its transfer into the metallic iron phase. Analysis of Figure 12b indicates that within the basicity range of 0.5 to 2.5, the slag viscosity increases with rising basicity. Nevertheless, all measured values remain lower than the viscosity at the basicity of 0.035. This implies that operation under high-basicity conditions can satisfactorily meet industrial production requirements.

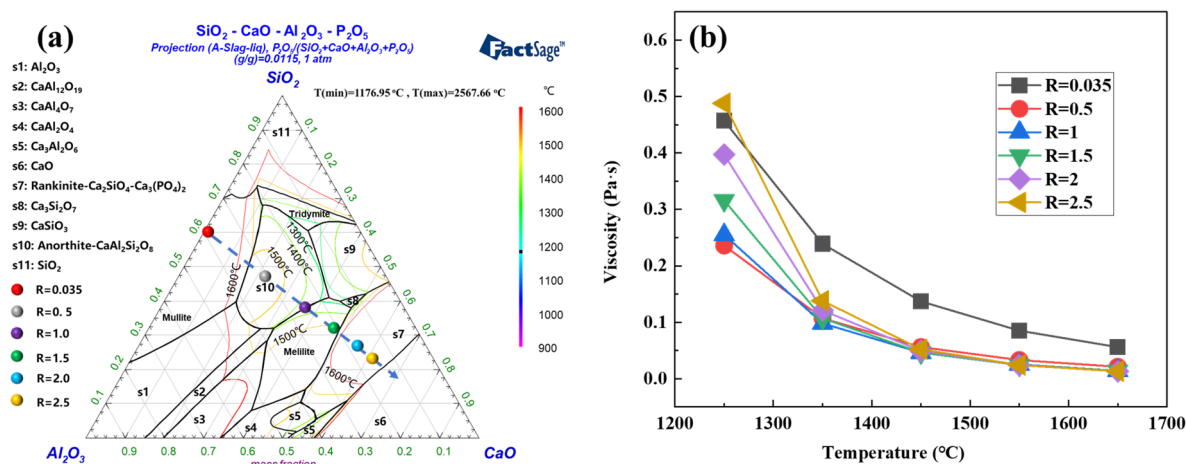


Figure 12. The high-temperature properties of the slag phase. (a) Liquid phase projection diagram; (b) viscosity of the slag phase.

As illustrated in Figure 13, the dephosphorization mechanism of the alkaline briquette direct reduction–smelting separation process involves three critical stages. Initially, the lattice activation of native $\text{Ca}_3(\text{PO}_4)_2$ occurs through interaction with the acidic SiO_2 - Al_2O_3 eutectic system, releasing highly reactive P_2O_5 components. Subsequently, thermally decomposed CaCO_3 generates active CaO that combines with P_2O_5 via interfacial ion-exchange reactions to reconstitute thermodynamically stable $\text{Ca}_3(\text{PO}_4)_2$ crystals. Ultimately, the regenerated $\text{Ca}_3(\text{PO}_4)_2$ forms a $\text{Ca}_2\text{Al}_2\text{SiO}_7$ - $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ - $\text{Ca}_3(\text{PO}_4)_2$ solid solution system, establishing a chemical barrier through dual inhibition effects (suppressing the decomposition of both native/regenerated calcium phosphate and phosphorus reduction), thereby achieving targeted phosphorus enrichment in the slag phase.

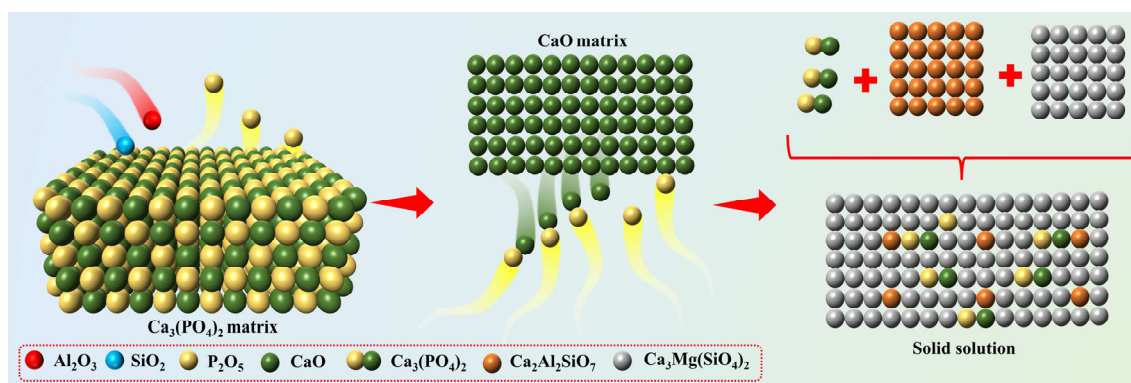


Figure 13. Schematic diagram of phosphorus removal by the direct reduction and melting separation processes of alkaline briquettes.

6. Conclusions

Through alkaline briquette direct reduction and smelting separation processes, low-phosphorus steel was successfully produced with supplementary MgO addition for enhanced desulfurization, ultimately yielding clean steel with ultralow phosphorus and sulfur levels. The main conclusions are as follows:

- (1) Process optimization demonstrated that coordinated regulation of the basicity ($R = 2$) and MgO dosage (5%) resulted in 98.56% iron content in the smelted metal phase, with phosphorus and sulfur reducing to 0.036% and 0.046%, respectively. The iron recovery reached 87.63%, accompanied by phosphorus and sulfur removal efficiencies of 94.67% and 90.56%, respectively, meeting standard steel composition requirements.

- (2) Slag characterization revealed that higher basicity facilitated phosphorus fixation as $\text{Ca}_3(\text{PO}_4)_2$ within $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$ matrices through solid solution formation. This spatial steric hindrance effect effectively suppressed phosphorus migration to the metallic phase, ensuring slag-phase phosphorus enrichment.
- (3) Thermodynamic analysis confirmed that under high basicity ($R \geq 2.0$), P_2O_5 activity markedly decreased via $\text{Ca}_3(\text{PO}_4)_2$ - Ca_2SiO_4 solid solution formation. This dual mechanism—inhibiting both calcium phosphate decomposition and phosphorus reduction—substantially enhanced system stability. The synergistic mechanism of “chemical immobilization coupled with thermodynamic stabilization” effectively addresses the fundamental challenges associated with achieving deep dephosphorization in high-phosphorus iron ores.

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