

## Article

# Development of Solid Waste-Based Composite Calcium Ferrite Flux and Its Application in Hot Metal Pre-Dephosphorization

Zheng Zhao <sup>1</sup>, Xiaoming Feng <sup>2</sup>, Yanling Zhang <sup>1,\*</sup> , Yao Zhang <sup>1</sup> and Yaoting Wu <sup>1</sup>

<sup>1</sup> State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China; suc\_zheng@163.com (Z.Z.)

<sup>2</sup> Jianlong Steel Holdings Co., Ltd., Beijing 100070, China

\* Correspondence: ustbzly1108@163.com

**Abstract:** To enhance the slagging efficiency of the lime-based slag system during the pre-treatment stage of hot metal, a composite calcium ferrite flux based on aluminum industry solid waste was developed in this study. The melting characteristics of the flux and its application in the pre-treatment of hot metal were investigated. The results indicated that the main phases of the composite calcium ferrite were  $\text{CaFe}_2\text{O}_4$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_5$ , and  $\text{Ca}_2(\text{Fe,Al})_2\text{O}_4$ . It exhibited high oxidation, high alkalinity, and a low melting point, thereby achieving excellent melting performance. Simulations of various dephosphorization fluxes in the pre-treatment of high-phosphorus hot metal, ordinary hot metal, and kilogram-scale dephosphorization experiment processes were conducted. Under the same experimental conditions, the composite calcium ferrite flux was able to achieve a dephosphorization rate of over 90% and a final phosphorus content of less than 0.02 wt% under high carbon content ( $[\%C] = 3.2 \text{ wt\%}$ ). In the application of hot metal pre-dephosphorization, this flux was able to achieve efficient melting and rapid slagging of lime at a lower temperature, and its slagging time was 50% faster than that of calcium ferrite flux. In addition, this flux enhanced the utilization efficiency of lime during the steelmaking process, effectively prevented the agglomeration of slag, and achieved efficient slag–metal separation. These characteristics were significantly better than the application effect of calcium ferrite flux. This flux has significant implications for the industrial application of deep dephosphorization in the pre-treatment stage of hot metal or the early stage of converter steelmaking.

**Keywords:** compound calcium ferrite flux; melting properties; hot metal pre-treatment; dephosphorization; solid waste disposal



**Citation:** Zhao, Z.; Feng, X.; Zhang, Y.; Zhang, Y.; Wu, Y. Development of Solid Waste-Based Composite Calcium Ferrite Flux and Its Application in Hot Metal Pre-Dephosphorization. *Materials* **2024**, *17*, 992. <https://doi.org/10.3390/ma17050992>

Academic Editor: Zhanjun Wang

Received: 16 January 2024

Revised: 11 February 2024

Accepted: 13 February 2024

Published: 21 February 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The pre-dephosphorization of hot metal or efficient dephosphorization in the early stages of converter smelting provided advantages for the production of low-phosphorus steel, while also reducing smelting costs and reducing slag emissions [1,2]. During the early stage of converter smelting, the temperature of the hot metal was low and the activity coefficient of [P] was high, which was thermodynamically very favorable for dephosphorization [3,4]. However, to enhance the efficiency of pre-dephosphorization, it is crucial to create favorable kinetic conditions, namely, the rapid dissolution of lime and the swift formation of a fluid initial slag [5,6]. This is particularly important in cases where the initial [Si] in hot metal is low (in blast furnace ironmaking processes, [Si] is often reduced to below 0.2% or even lower to decrease the fuel ratio) or where there is a high proportion of scrap steel and insufficient heat. The use of effective fluxes that promote lime dissolution becomes crucial.  $\text{CaF}_2$  is an effective flux to promote the dissolution of lime, but due to its potential hazards to the environment and human health, it has been widely banned [7]. Currently, the development of fluoride-free efficient fluxes has received much attention.

Numerous studies have shown that  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  significantly promote the dissolution of lime. Diao et al. [8] added small amounts of  $\text{Na}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  to fluoride-free  $\text{CaO-FeO-SiO}_2$  slag to reduce the melting point and enhance dephosphorization reactions. With only 0.7 to 3.1% w( $\text{Na}_2\text{O}$ ) in the dephosphorization slag, a dephosphorization rate of 81.4 to 90.7% was achieved. Du et al. [9] found that  $\text{Na}_2\text{O}$  reduced the activity coefficient of  $\text{P}_2\text{O}_5$  in steelmaking slag and can substitute for  $\text{CaO}$  in the solid solution to form  $2\text{CaO}\cdot\text{SiO}_2\text{-Na}_2\text{O}\cdot 2\text{CaO}\cdot\text{P}_2\text{O}_5$  ( $\text{C}_2\text{S-N}_2\text{C}_2\text{P}$ ), increasing the distribution ratio of  $\text{P}_2\text{O}_5$  in the slag. Our team [10,11] previously proposed using red mud rich in  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$ , generated by the alumina industry, as a steelmaking flux. Semi-industrial trials at the 200 kg scale demonstrated that even at high [%C] contents of 2 to 3 wt%, a dephosphorization rate of over 90% and an endpoint [%P] content of 0.02 wt% were still achieved. However, these substances are not suitable for use in the early stages of converter steelmaking or when the hot metal temperature is low, as their high melting points ( $>1300^\circ\text{C}$ ) hinder rapid melting under hot metal temperatures. Only after melting and releasing components, such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$ , do they effectively promote the dissolution of lime.

Calcium ferrite, an excellent fluoride-free flux, has a low melting point and rapidly forms a highly oxidative and alkaline initial slag [12–14]. Sukenaga et al. [15] found that the viscosity of a slag system with 19 wt%  $\text{CaO}$  and 81 wt%  $\text{FeO}_x$  was 0.065 Pa·S, significantly lower than the 2.4 Pa·S of a  $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3$  system, suggesting that a more fluid slag system can facilitate phosphorus transfer to the slag. The studies conducted by Jeon et al. [12] and Lee et al. [16] illuminated the synthesis of calcium ferrite melts. Their findings underscored the crucial role of oxygen partial pressure and iron oxide morphology in influencing the formation kinetics of  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . Furthermore, they demonstrated that the sintering temperature could be effectively reduced to a range of  $1000\text{--}1100^\circ\text{C}$  by incorporating a specific quantity of  $\text{Al}_2\text{O}_3$  into the calcium ferrite, thereby facilitating the formation of Calcium Aluminum Ferrite (CAF). Lee et al. [13] investigated the mechanism and impact of calcium ferrite flux on lime melting, noting that when lime surfaces were coated with iron oxides compared to uncoated samples, more low-melting-point calcium ferrite phases formed, reducing the mechanical properties of lime and making it more easily dissolved in steelmaking slag. Studies by Sato et al. [3] and Mi et al. [17] showed that, due to its low melting point and highly oxidizing capabilities, calcium ferrate was a suitable agent for use in hot metal dephosphorization tests. These tests achieved high dephosphorization rates, nearly 90%, at lower temperatures and in the presence of high levels of [%C]. Wu et al. [1,14] used iron oxide scale and lime-synthesized calcium ferrite in industrial hot metal dephosphorization trials, revealing that calcium ferrite reduced the melting temperature of slag and increased the amount of slag in the double-slag process. The average dephosphorization rate of hot metal with calcium ferrite slag was 88.06%, and the average melting temperature was  $1137^\circ\text{C}$ , superior to the 77.7% dephosphorization rate and  $1296^\circ\text{C}$  melting temperature of fluorspar slag. Moreover, Table 1 summarizes the variety of melts synthesized from solid wastes, along with their respective applications. Generally, these fluxes are classified into non-pre-melting and pre-melting types. The common disadvantage of non-pre-melting fluxes lies in their high melting point, necessitating more heat absorption during the melting process. The disadvantages of pre-melted fluxes include either the high cost of raw materials or the complexity and difficulty of the preparation process. It is anticipated that the use of these fluxes may prove challenging to popularize. Calcium ferrate is considered the best flux to replace  $\text{CaF}_2$  due to its significant advantages in slag forming and hot metal dephosphorization. However, calcium ferrite products are currently rare in the market, mainly due to the high cost of the raw materials (typically fine ore powder and lime) and preparation. Steel producers urgently need to find a flux with similar fluxing effects but at a relatively lower preparation cost.

**Table 1.** Fluxes prepared from solid wastes and their applications.

| Solid Waste Material   | Composites           | Preparation Methods                                                                           | Properties                                              | Refs.      |
|------------------------|----------------------|-----------------------------------------------------------------------------------------------|---------------------------------------------------------|------------|
| Red Mud                | Flux                 | Room temperature, red mud as an additive                                                      | Dephosphorization, desulfurization                      | [10,11,18] |
| Red Mud                | Flux                 | Room temperature, briquette of red mud mixed with lime powder                                 | Dephosphorization and desiliconization                  | [5,19]     |
| Red Mud                | Flux                 | High-temperature pre-reduction, red mud mixed with graphite powder                            | Desulfurization                                         | [20,21]    |
| Red Mud                | Flux                 | High-temperature roasting, red mud mixed with iron ore powder                                 | Metallurgical properties (reducibility, strength, etc.) | [22,23]    |
| Mill scales            | Calcium ferrate flux | High-temperature roasting, mill scales mixed with lime                                        | Dephosphorization                                       | [1,14]     |
| Desulfurization gypsum | Calcium ferrate      | High-temperature roasting, desulfurization gypsum, graphite powder mixed with iron ore powder | Desulfurization, sintering                              | [24]       |

In this study, red mud, enriched in  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  and produced by alumina companies, was used to develop a flux primarily composed of calcium aluminoferrite. The melting characteristics and deep dephosphorization effectiveness of the new fluxes for the hot metal pre-treatment process were analyzed and compared with conventional lime slagging agents and calcium ferrite fluxes. The aim was to provide significant guidance for the cost-effective industrial application of this novel flux in the pre-treatment of hot metal or the early stages of converter steelmaking.

## 2. Thermodynamic Analysis of Flux Preparation

The optimal conditions for pre-dephosphorization of hot metal theoretically involve a lower reaction temperature, along with the formation of highly alkaline and strongly oxidizing slag. The development of fluorine-free dephosphorizing fluxes, characterized by a low melting point, high alkalinity, and superior oxidizing capacity, presents an extremely attractive proposition [1,3,5]. Figure 1a–d displays the phase diagrams generated using the thermodynamic software FactSage8.3 for  $\text{CaO-CaF}_2$ ,  $\text{CaO-Fe}_2\text{O}_3$ ,  $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ , and  $\text{CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-5\%Na}_2\text{O}$ .  $\text{CaF}_2$  significantly enhances the dissolution of lime primarily because it forms low-melting-point compounds with  $\text{CaO}$ , with the lowest melting point being  $1314^\circ\text{C}$  [25]. Consequently, the addition of  $\text{CaF}_2$  during the steelmaking process was found to promote the rapid melting of lime. In the  $\text{CaO-Fe}_2\text{O}_3$  phase diagram (Figure 1b), the lowest melting point, at  $1216^\circ\text{C}$ , occurs when  $\text{CaFe}_2\text{O}_4$  forms at a molar ratio of about 1:1 with  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ , which is lower than typical hot metal temperatures [12]. Figure 1c shows that adding  $\text{Al}_2\text{O}_3$  to the  $\text{CaFe}_2\text{O}_4$  phase further reduces its melting point to  $1142^\circ\text{C}$ , with a composition of approximately 18% $\text{CaO}$ , 9% $\text{Al}_2\text{O}_3$ , and 73% $\text{Fe}_2\text{O}_3$ . Adding  $\text{Na}_2\text{O}$  to this composition further reduces the melting point to around  $1041^\circ\text{C}$ , as shown in Figure 1d, with the mineral phases being  $\text{Ca}(\text{Al,Fe})_2\text{O}_4$ ,  $\text{Ca}(\text{Al,Fe})_6\text{O}_{10}$ ,  $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$ , and Slag-liq. Analyzing different systems' phase diagrams reveals a pattern: the lowest liquid-phase temperature in binary phase diagrams is found in the mineral structures of  $\text{CaFe}_2\text{O}_4$ ,  $\text{CaFe}_4\text{O}_7$ , and  $\text{Ca}_2\text{Fe}_2\text{O}_5$ . When new components  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  are added, isomorphic new solid solutions of calcium ferrite phases such as  $\text{Ca}(\text{Al,Fe})_2\text{O}_4$ ,  $\text{Ca}(\text{Al,Fe})_6\text{O}_{10}$ , and  $\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$  can form, or Na-containing solid solutions and liquid slag phases may develop [9,16,26]. Numerous studies [26] have confirmed that  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  have similar ionic radii and charge balance, allowing them to occupy the same positions in the lattice without changing the structure. The formation of  $\text{Na}^+$  solid solutions is more related to the substitution of  $\text{Ca}^{2+}$ , as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  have similar ionic radii, and the substitution does not affect the phase structure [9]. In conclusion, calcium aluminoferrite materials containing  $\text{Na}_2\text{O}$  have a melting point far below the temperature of hot metal, and as Figure 1c,d shows, these materials contain a considerable amount of  $\text{Fe}_2\text{O}_3$ . When added to hot metal

along with lime, they can create highly favorable thermodynamic and kinetic conditions for the pre-dephosphorization of hot metal.

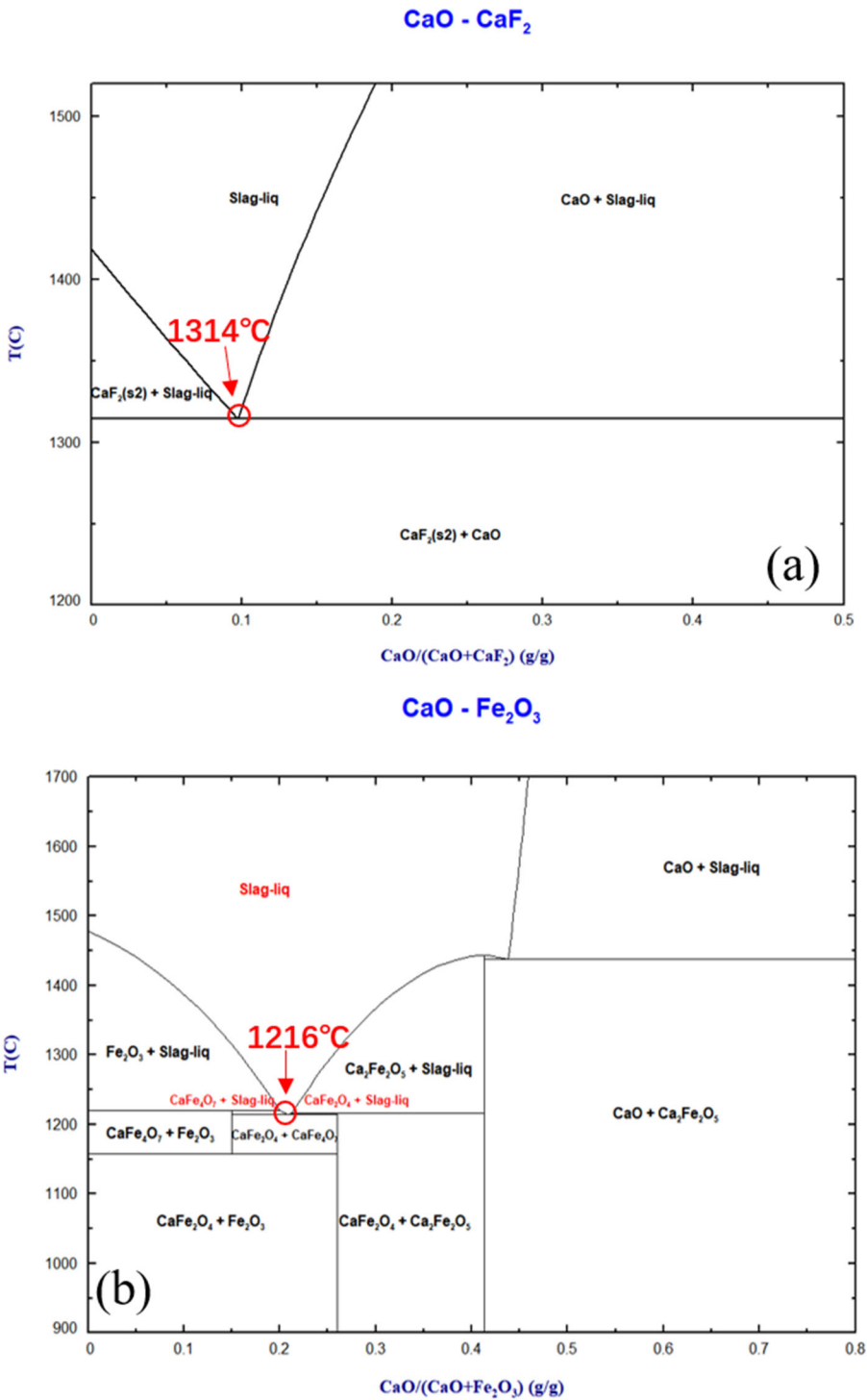


Figure 1. Cont.

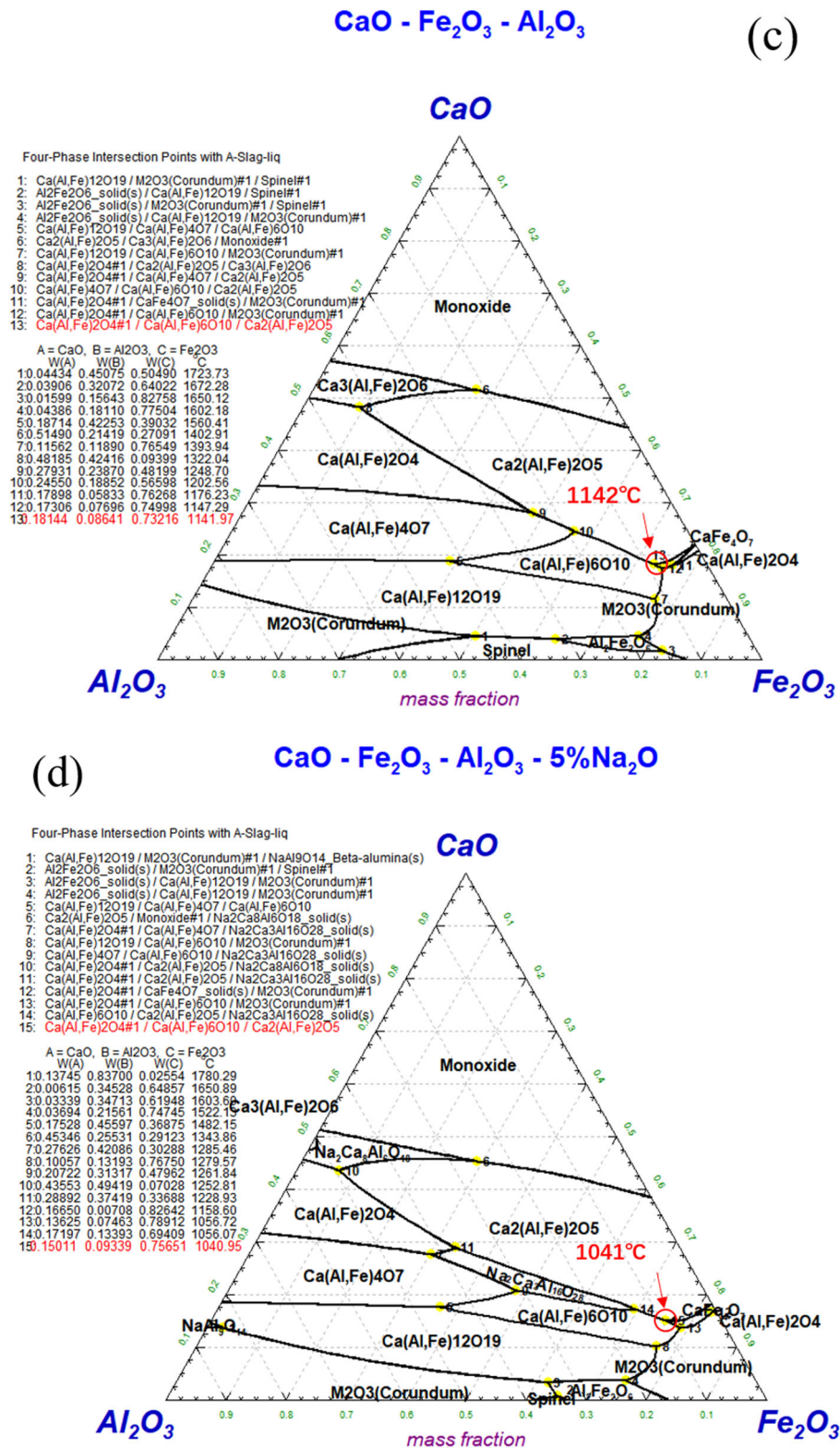


**Figure 1.** Mineral phase design based on (a) CaO-CaF<sub>2</sub>, (b) CaO-Fe<sub>2</sub>O<sub>3</sub>, (c) CaO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, and (d) CaO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-5%Na<sub>2</sub>O phase diagrams. The yellow circles are added by the software itself and represent intersections between different phases.

### 3. Experimental

#### 3.1. Materials

In this study, red mud sourced from an alumina company, which had undergone magnetic separation (Table 2), was used as the raw material. A specific proportion of lime (Table 2) was added and mixed uniformly. After sintering at 1100 °C for 2 h in a muffle furnace, a composite calcium ferrite, referred to as SW-CAF in this paper, was successfully synthesized. Its chemical composition is presented in Table 2. Additionally, following the current standard YBT-4266-2011 for metallurgical CF-65 type physicochemical indicators, laboratory synthesis of calcium ferrite flux (CF-65) was conducted using  $\text{Fe}_2\text{O}_3$  and lime, which were gradually cooled to room temperature after being held at 1250 °C for 2 h, with the composition detailed in Table 1. Both fluxes were prepared under air atmosphere and the heating rate for the ramp-up was set to 8 °C/min. The pig iron used for the dephosphorization experiments was obtained from a specific company, with its composition shown in Table 3. High-phosphorus pig iron was prepared by adding a ferrophosphorus reagent (Table 3) to the base pig iron, as indicated in Table 3. Before the experiments, all materials were dried at 110 °C to a constant weight.

**Table 2.** Experimental raw material composition (wt%).

| Material                     | $\text{Fe}_2\text{O}_3$ | $\text{Al}_2\text{O}_3$ | CaO   | $\text{SiO}_2$ | $\text{TiO}_2$ | $\text{Na}_2\text{O}$ | $\text{K}_2\text{O}$ | LOI   |
|------------------------------|-------------------------|-------------------------|-------|----------------|----------------|-----------------------|----------------------|-------|
| Red mud                      | 75.5                    | 13.6                    | 0.49  | 2.49           | 4.64           | 2.06                  | 0.02                 | 15.35 |
| SW-CAF                       | 50.74                   | 10.29                   | 30.46 | 1.76           | 3.46           | 1.38                  |                      |       |
| CF-65                        | 68                      | 1.3                     | 23    | 2.5            |                |                       |                      |       |
| Lime(AR)                     |                         |                         | 99.8  |                |                |                       |                      |       |
| $\text{Fe}_2\text{O}_3$ (AR) | 99.8                    |                         |       |                |                |                       |                      |       |

**Table 3.** Iron initial composition (wt%).

| Material                 | C    | Si   | Mn   | P     | S    |
|--------------------------|------|------|------|-------|------|
| Pig iron                 | 4.10 | 0.40 | 0.32 | 0.14  | 0.04 |
| FeP(AR)                  | 0.13 | 0.38 | 1.07 | 21.49 | 0.06 |
| High phosphorus pig iron | 4.10 | 0.40 | 0.32 | 0.25  | 0.04 |

#### 3.2. Equipment and Procedures

##### 3.2.1. Melting Temperature Measurement

The melting points of the synthesized fluxes CF-65 and SW-CAF were tested using a high-temperature reaction in situ observation and online analysis system [27,28], as depicted in Figure 2a–c. This system comprises a three-dimensional super-depth-of-field high-temperature video microscope (CCD), a high-temperature microscope for contact angle measurement, and a high-temperature furnace, equipped with the HiTOS observation and control system for real-time in situ video imaging and data recording. The high-temperature furnace uses a halogen light source for heating, with a maximum temperature rise/fall rate of 1000 °C/min. The procedure was as follows: first, the CF-65 and SW-CAF flux samples were ground to powders of less than 80  $\mu\text{m}$ , then molded into cylindrical shapes of  $\Phi 3 \text{ mm} \times \text{H}4 \text{ mm}$  using a mold, as shown in Figure 2a, and placed on a rectangular MgO piece with dimensions of  $\text{H}1.5 \text{ mm}$ . Subsequently, the MgO piece was placed on the furnace chamber rack for heating, as illustrated in Figure 2b. The heating regime during the testing phase controlled the temperature rise/fall rate at 20 °C/min. The melting of the fluxes underwent three stages: overall shrinkage, the beginning of liquid phase formation with solid-liquid coexistence, and complete liquefaction. The melting temperature was determined by the temperature at the initial moment when the height became constant after complete liquefaction, as shown in Figure 2c, corresponding to the fourth step in the material melting process (the temperature is displayed in the upper left corner).

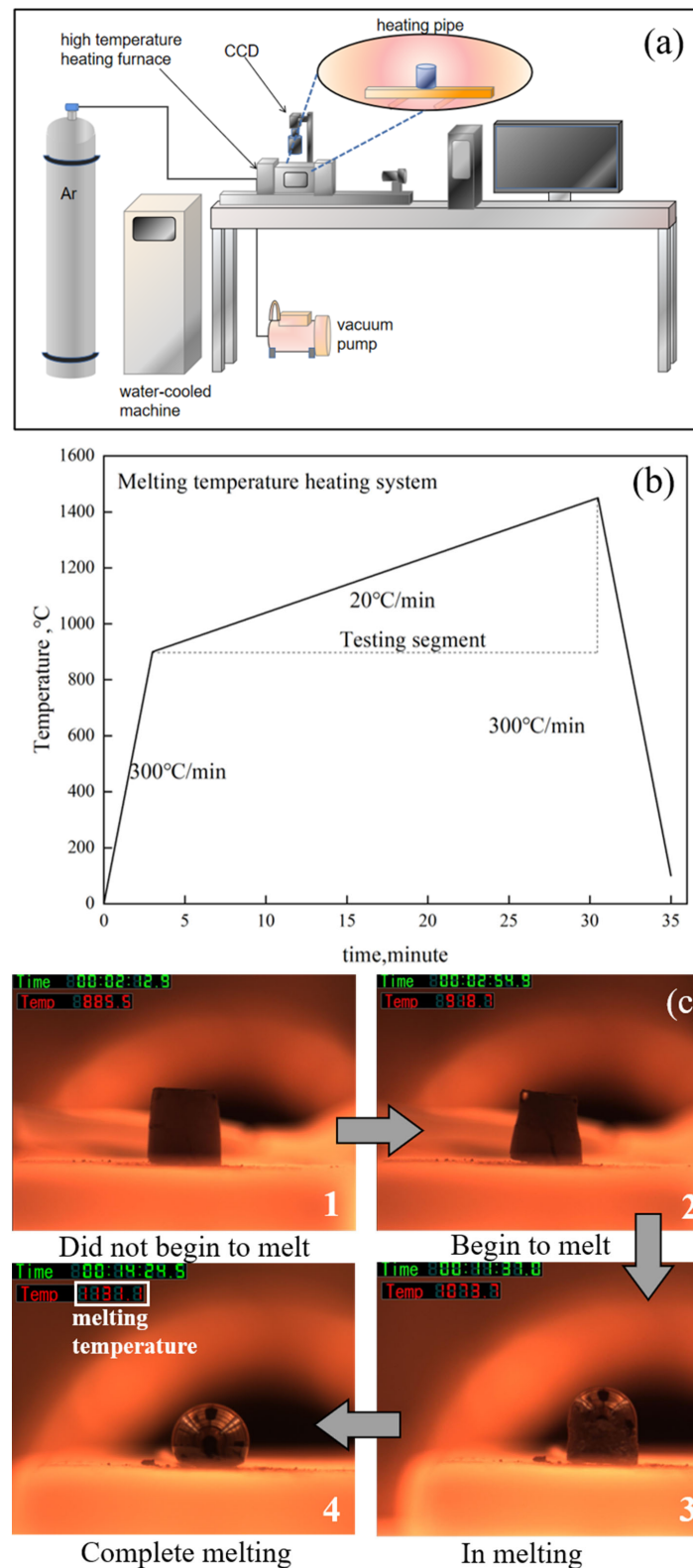


**Figure 2.** (a) The high-temperature reaction in situ observation system, (b) the heating regime for melting temperature tests, (c) and the testing process of melting temperature. The arrows are guides to the next step and the numbers represent the steps and flow.

### 3.2.2. Hot Metal Dephosphorization

- (1) Laboratory experiment: The dephosphorization pre-treatment of hot metal was conducted in a  $\text{MoSi}_2$  resistance furnace. Throughout the experiment, argon gas (99.9%)

was introduced from the top of the vertical furnace to prevent oxidation of the hot metal and maintain a relatively stable oxygen partial pressure and atmosphere. Initially, the pig iron was heated from room temperature to 300 °C at a rate of 25 °C/min and then to 1410 °C at a rate of 8 °C/min (for the high-phosphorus group, pre-weighed FeP was added to the melt). After maintaining the sample at 1410 °C for 20 min to ensure uniform temperature, a sample weighing 20–25% of the hot metal, approximately 245 g, was added to the surface of the molten metal.

- (2) Experiment with a 10 kg induction furnace: To emulate industrial trial conditions, the initial sample addition in the induction furnace was determined to cover the surface of the molten steel, approximately 13% of the hot metal weight. During the experiment, 2.3 kg of pig iron was heated in a magnesia crucible from room temperature to 1410 °C. Once the hot metal was completely molten, the temperature was held constant for 5 min to collect initial samples. Under three experimental conditions, mixtures of (CaO+Fe<sub>2</sub>O<sub>3</sub>), (CaO+Fe<sub>2</sub>O<sub>3</sub>+CF), and (CaO+Fe<sub>2</sub>O<sub>3</sub>+CAF) were added to the surface of the molten metal and reacted for 5 min before collecting steel and slag samples. The reaction continued for additional periods of 10, 15, and 20 min, after which steel and slag samples were collected, and the steel was cast at high temperatures.

Post-experiment, the crucibles containing the quenched samples were placed in an oven to completely dry. The slag and pig iron were physically separated for subsequent sample analysis.

### 3.2.3. Experimental Scheme of Pre-Dephosphorization

The experimental scheme is presented in Table 4. It includes trials H1 to H3 and L1 to L3, which utilize high-phosphorus iron with an initial phosphorus content (P<sub>0</sub>) of approximately 0.25 wt% and regular iron with a P<sub>0</sub> of about 0.15 wt%, respectively, for preliminary dephosphorization laboratory tests. Experiment G3, using standard pig iron and conducted in a 10 kg induction furnace, follows the same protocol as H3 and L3. Its purpose is to further assess the efficacy of SW-CAF in the preliminary dephosphorization of hot metal. In experiments H1 and L1, no flux is added; lime and Fe<sub>2</sub>O<sub>3</sub> are the sole dephosphorization agents. Other trial groups are formulated by adding various types of flux to the CaO and Fe<sub>2</sub>O<sub>3</sub> base. It is important to note that in all experiments, the composition of the dephosphorization agent remains constant, with the total mass ratios of CaO to Fe<sub>2</sub>O<sub>3</sub> being identical.

**Table 4.** The experimental scheme of the hot metal pre-dephosphorization process (wt%).

| No. | Slag Material |                                |       |        | [P] <sub>0</sub> in Hot Metal | Experimental Equipment    |
|-----|---------------|--------------------------------|-------|--------|-------------------------------|---------------------------|
|     | CaO           | Fe <sub>2</sub> O <sub>3</sub> | CF-65 | SW-CAF |                               |                           |
| H1  | 15.1%         | 84.9%                          |       |        | 0.21~0.25                     | MoSi <sub>2</sub> furnace |
| H2  | 13.7%         | 61.3%                          | 25%   |        |                               |                           |
| H3  | 13.7%         | 61.3%                          |       | 25%    |                               |                           |
| L1  | 15.1%         | 84.9%                          |       |        | 0.14                          |                           |
| L2  | 13.7%         | 61.3%                          | 25%   |        |                               |                           |
| L3  | 13.7%         | 61.3%                          |       | 25%    |                               |                           |
| G3  | 13.7%         | 61.3%                          |       | 25%    | 0.15                          | Induction furnace         |

### 3.3. Analysis

The structures, the prepared materials, and the slag samples were characterized by using an X-ray diffract meter (XRD, Rigaku, SmartLab, Tokyo, Japan). The composition of the samples was analyzed using X-ray fluorescence spectroscopy (XRF, PANalytical, AX-IOSmAX, Almelo, Netherlands). A 1 g metal sample was used to determine the [C] content with a carbon/sulfur analyzer (CS, Eltra, CS-800, Haan, Germany). A 0.1 g sample was completely dissolved in a solution of 3 mol/L HCl and 1 mol/L HNO<sub>3</sub>, and the [P] content was then determined using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS,

Thermo Scientific, ICAP RQ, Waltham, MA, USA). The microstructure and properties of the dephosphorized slag were determined by scanning electron microscope energy dispersive spectrometry (SEM-EDS, FEI, MLA250, Hillsboro, OR, USA).

## 4. Results

### 4.1. Phase and Melting Properties of CF and SW-CAF

Figure 3a,b, respectively, display the XRD phases and melting characteristics of two types of fluxes. Figure 3a revealed that the synthetic calcium ferrite flux CF-65 was primarily composed of  $\text{CaFe}_2\text{O}_4$  and  $\text{Ca}_2\text{Fe}_2\text{O}_4$ . These mineral phases had low melting points and were characterized by high oxidizing properties and high alkalinity. The predominant phases in SW-CAF were  $\text{CaFe}_2\text{O}_4$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_4$ , and  $\text{Ca}_2(\text{Fe,Al})_2\text{O}_4$ . In addition to the calcium ferrite mineral phases, this flux also contained calcium iron aluminate phases, collectively referred to as composite calcium ferrite phases.

As shown in Figure 3b, the melting temperatures of both fluxes were below  $1300^\circ\text{C}$ , which was sufficient to achieve a complete liquid phase under the temperature requirements for desiliconization and dephosphorization of hot metal ( $1250\sim 1450^\circ\text{C}$ ). The melting temperature of flux CF-65 stood at  $1253^\circ\text{C}$ , while that of SW-CAF was  $1186^\circ\text{C}$ . During the high-temperature melting process, CF-65 started deforming at  $1184^\circ\text{C}$ , transitioned from a solid to a flowing liquid phase at  $1195^\circ\text{C}$ , and took 186 s to fully liquefy. In contrast, SW-CAF began deforming at  $1053^\circ\text{C}$ , initiated the transition at  $1141^\circ\text{C}$ , and required 147 s to fully liquefy. In summary, the melting temperature of the composite calcium ferrite was significantly lower than that of the synthetic calcium ferrite, melting more rapidly and showing superior fluidity. This rendered it suitable as a flux in the pre-treatment stage of hot metal.

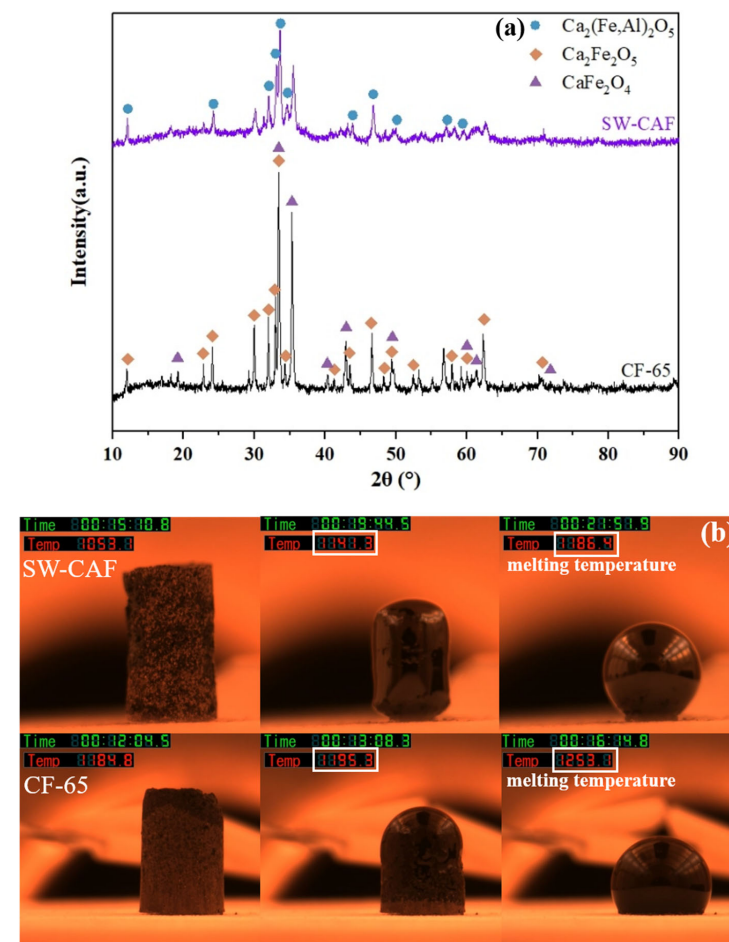


Figure 3. (a) XRD patterns and (b) melting characteristics of different fluxes.

#### 4.2. Dephosphorization Test Results

Under high-phosphorus and regular iron conditions, three types of slag materials were used for the pre-dephosphorization of hot metal:  $\text{CaO}+\text{Fe}_2\text{O}_3$ ,  $\text{CaO}+\text{Fe}_2\text{O}_3+25\%\text{CF}$ , and  $\text{CaO}+\text{Fe}_2\text{O}_3+25\%\text{CAF}$ . The variations in the [P] and [C] contents in the metal over time are shown in Figure 4a,b. It was evident that, under similar temperatures and slag-making regimes, slags containing composite calcium ferrite demonstrated significant dephosphorization effectiveness, followed by those containing calcium ferrite, both surpassing the conventional  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag system. This trend was consistent across different initial [%P] contents in the hot metal. Specifically, with high initial phosphorus, the [%P] content in the  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag only reduced from 0.25 wt% to 0.12 wt% within 10 min, while the final [%P] in the  $\text{CaO}+\text{Fe}_2\text{O}_3+25\%\text{CF}$  slag lowered to 0.095 wt% from 0.25 wt%. The composite calcium ferrite slag reduced [%P] from 0.21 wt% to 0.022 wt% within a short 10 min span, significantly lower than the first two. When the initial [%P] was around 0.14 wt%, after 10 min of dephosphorization, the final phosphorus contents in the three slag systems were 0.087 wt%, 0.063 wt%, and 0.01 wt%, respectively, with the composite calcium ferrite slag achieving the lowest final phosphorus content.

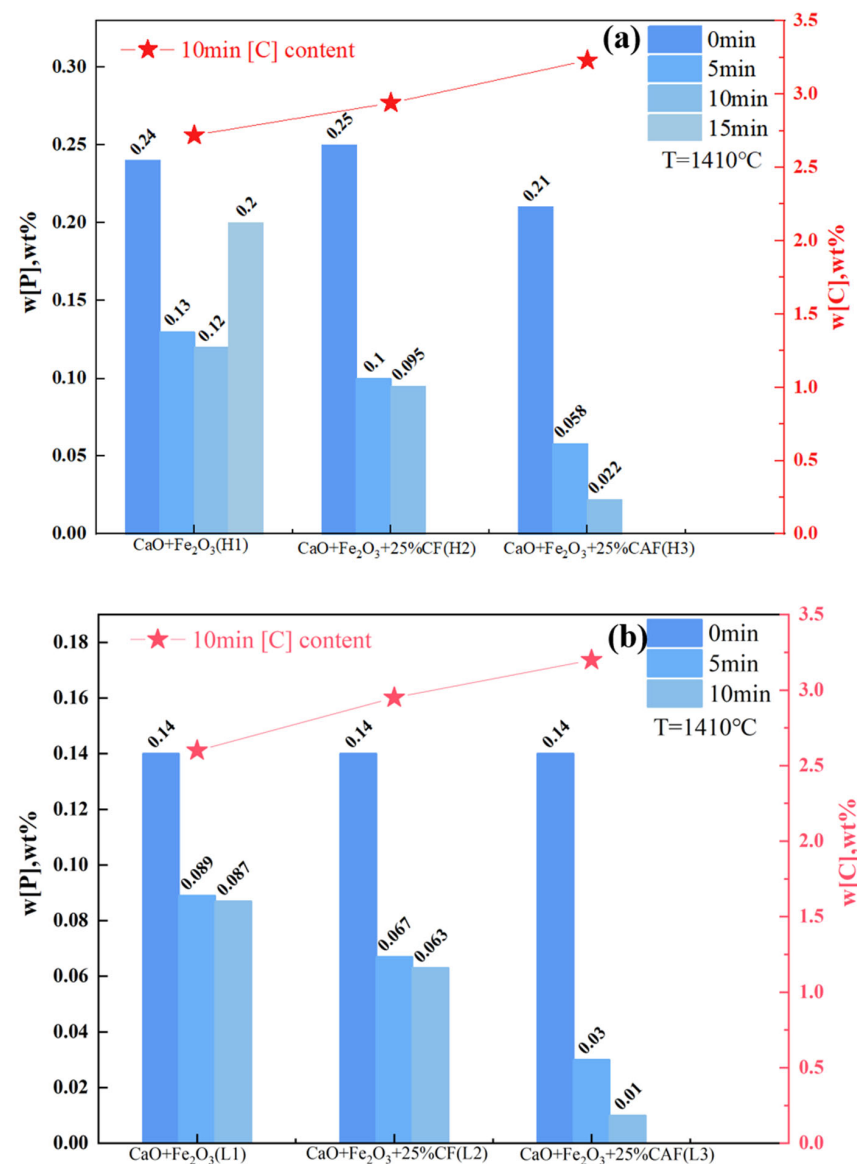


**Figure 4.** Dephosphorization effects of different flux types under (a) high-phosphorus and (b) regular iron conditions.

Notably, when the phosphorus content in the hot metal was high, the  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag experienced severe rephosphorization at 15 min, attributed to a rapid depletion of  $\text{FeO}$ , leading to a rise in the slag melting point and reduced fluidity. The CF-containing slag system did not exhibit rephosphorization between 10 and 15 min but lost its dephosphorization capacity, achieving a maximum dephosphorization rate of only 62%. The flux in this study maintained a strong dephosphorization ability even after 10 min, reaching a dephosphorization rate of 90%. This was attributed to components such as  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$  in the slag, which maintained good fluidity even with reduced  $\text{FeO}$  concentration.

The  $[\text{C}]$  content during the iron dephosphorization stage was crucial. The  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag system exhibited the highest  $[\text{C}]$  consumption, while the CAF-containing slag had the lowest, with a final  $[\text{C}]$  content of 3.2 wt%. This study effectively achieved “dephosphorization while preserving carbon,” attributed to the slag system’s superior dephosphorization kinetics under low-temperature conditions, thus enhancing thermodynamic dephosphorization. In the  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag system, when dephosphorization kinetics were poor,  $[\text{P}]$  accumulated at the slag–metal interface and could not diffuse rapidly, creating a local equilibrium. Under these conditions,  $(\text{FeO})$  in the slag tended to react with  $[\text{C}]$ , consuming the  $[\text{C}]$  in the hot metal. The flux in this study successfully achieved deep dephosphorization under high  $[\text{C}]$  conditions, which was significant for the pre-treatment stage of hot metal or early in converter steelmaking.

Figure 5 shows the pre-dephosphorization experiment (G3) in a 10 kg induction furnace. The hot metal temperature was  $1410^\circ\text{C}$ , and under conditions without stirring or oxygen blowing, the initial  $[\text{P}]$  was 0.152 wt%. After 20 min, the  $[\text{P}]$  in the metal was 0.0316 wt%, achieving a dephosphorization rate of 79.2%, without any rephosphorization. Compared to the initial  $[\text{P}]$  of 0.14 wt% in the laboratory experiments, the difference in dephosphorization after 10 min, resulting in the  $[\text{P}]$  of 0.01 wt%, was primarily due to varying slag amounts and significant differences in slag surface temperatures. After adding the slag, it took approximately 3 min to form, and the slag still exhibited some fluidity after 20 min of the dephosphorization reaction. The final slag contained 4.7 wt%  $\text{P}_2\text{O}_5$  and had a binary basicity of about 3.2 (Table 5). Despite the deeper melt pool, lower surface temperatures, and reduced slag amount—factors generally unfavorable for dephosphorization—the process still achieved a final phosphorus content below 0.04 wt% within 15 min, meeting the requirements for most plain carbon steel productions. Thus, the experiment overall replicated the results of the low melting temperature and high dephosphorization rate characteristic of composite calcium ferrite flux.

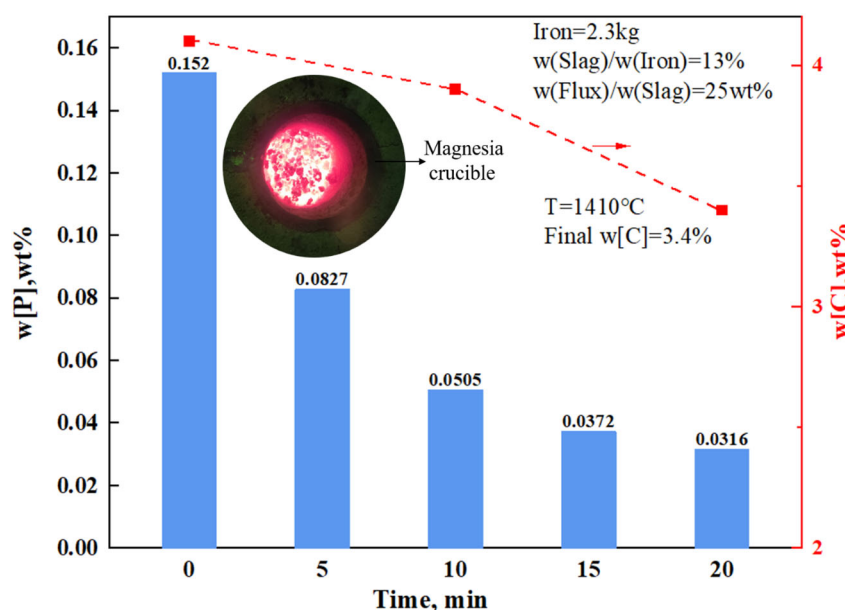


Figure 5. A kilogram-scale experiment.

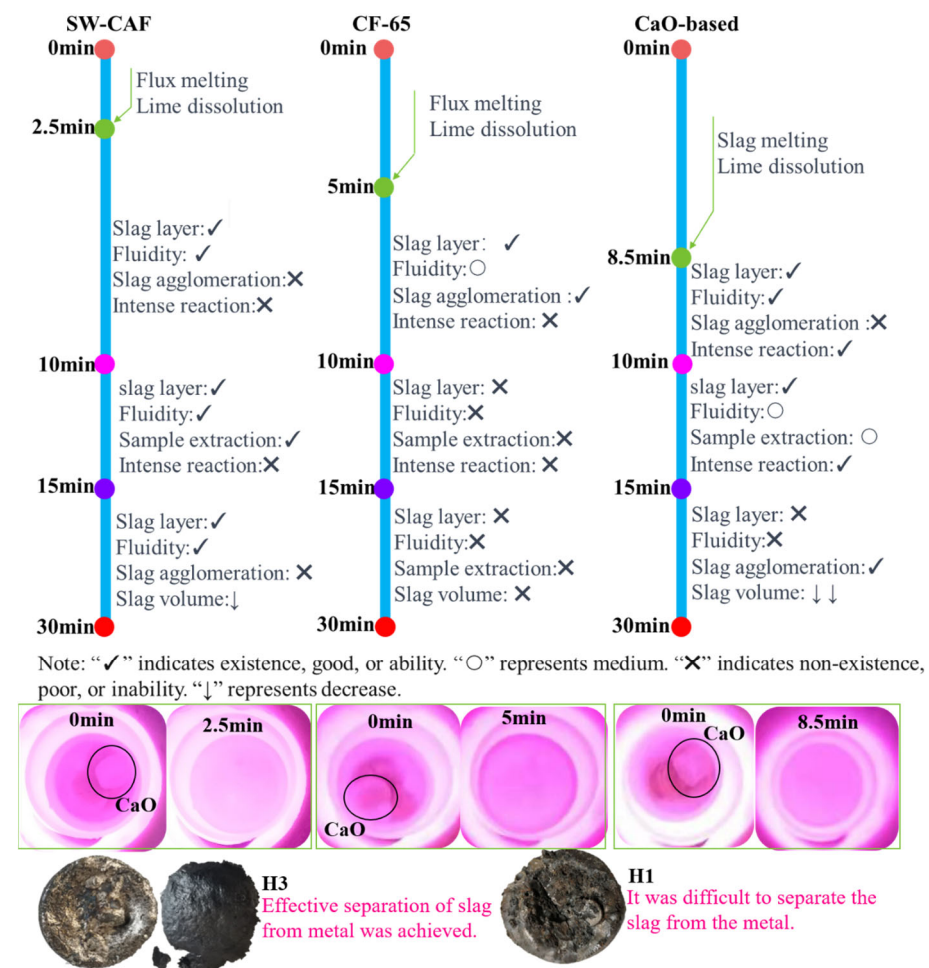
**Table 5.** The final slag composition (wt%).

| Slag | CaO  | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> |
|------|------|------------------|--------------------------------|--------------------------------|------------------|-------------------|-------------------------------|
| G3   | 32.9 | 10.1             | 34.5                           | 6.11                           | 2.24             | 0.741             | 4.70                          |

## 5. Discussion

### 5.1. The Slag Formation Process of Different Fluxes

Figure 6 depicts the slag formation within 30 min during the experiment for three different slag systems under the same hot metal conditions. All lime briquettes, Fe<sub>2</sub>O<sub>3</sub> briquettes, and flux particles maintained the same size at the beginning and were simultaneously added to the surface of the hot metal. Regarding lime dissolution time, in the slag with added composite calcium ferrite flux, the lime dissolved completely in the shortest time, taking only 2.5 min. In contrast, in the CaO+Fe<sub>2</sub>O<sub>3</sub> slag system without any added flux, the lime took 8.5 min to fully disappear. Compared to the conventional slag system, the slag formation time with the addition of the flux in this study was over 70% faster.

**Figure 6.** The melting phenomena of different slagging materials.

Regarding the relationship between slag formation and dephosphorization efficiency, during the dephosphorization process in the CaO+Fe<sub>2</sub>O<sub>3</sub> slag system, the slag became completely liquid 8.5 min after adding the slagging agent. At 10 min into the reaction, slag–metal reaction behavior manifested as intense splashing. As depicted in Figure 4a, for the H1 group at 10 min, the phosphorus content in the metal ([%P] = 0.12 wt%) was relatively high, indicating poor dephosphorization due to the short time that lime participated in the reaction after dissolving, and rephosphorization occurred in the latter 15 min.

For the slagging agent containing CF flux, the calcium ferrite flux melted within 5 min and quickly completed melting, after which CaO was immediately dissolved in the liquid slag. At 10 min into the reaction, a small amount of precipitate was observed in the slag, and fluidity began to decline. As shown in Figure 4a, for the H2 group at 10 min, the phosphorus content ( $[\%P] = 0.095 \text{ wt\%}$ ) was slightly lower than the H1 group, attributed to increased slag reaction time after slag formation. However, after 15 min, the slag layer had disappeared, and agglomeration and clumping occurred, a phenomenon referred to as “re-drying”. For the slagging agent containing CAF flux, the flux melted into liquid slag within 2.5 min, followed by rapid dissolution of CaO in the liquid slag. At 10 min into the reaction, the slag–metal reaction continued, with a visible flowing slag layer. As shown in Figure 4a, for the H3 group at 10 min,  $[\%P]$  had already reduced to  $0.022 \text{ wt\%}$ . The advantage of this flux was in prolonging the re-drying period, with almost no slag-state re-drying, thereby enhancing dephosphorization efficiency.

It was noteworthy that the early dephosphorization effects within 5 min for groups H1 to H3, as shown in Figure 4a, where the  $[\%P]$  for group H3 (using composite calcium ferrite flux) was significantly lower at  $0.058 \text{ wt\%}$  compared to the H1 and H2 groups. This demonstrated the advantage of the flux’s pre-melting and early slag formation, indicating that a lower melting point leads to faster early slag formation, thus advancing the dephosphorization phase. The dephosphorization pattern was consistent with that of high-phosphorus hot metal.

In discussing the relationship between slag formation, the slag–metal separation interface, and the carbon content, when the dephosphorization process continued for 30 min, the slag with CAF flux, despite the reduced volume, maintained good fluidity. The fluidity of the slag system containing CF flux significantly decreased, introducing complexities to the sampling task. For the  $\text{CaO}+\text{Fe}_2\text{O}_3$  slag system, the slag was re-dried, reducing the fluidity of the steel. As depicted in Figures 4a and 6, the steel block from group H3, subsequent to water quenching, exhibited a smooth surface, suggestive of a more comprehensive slag–metal separation. In contrast, the steel block from group H1 presented an uneven surface, which hindered effective slag–metal separation, akin to the observations in the H2 group. Considering the coverage of the slag layer over the steel during the reaction, the final  $[\text{C}]$  content for the H3 group was  $3.23 \text{ wt\%}$ , while it was  $2.72 \text{ wt\%}$  and  $2.94 \text{ wt\%}$  for the H2 and H1 groups, respectively. In conclusion, the slag with added composite calcium ferrite flux had rapid slag formation, efficient lime dissolution, and good slag–metal separation, all of which played a crucial role in enhancing deep dephosphorization capability. Moreover, the presence of multiple components such as  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}/\text{TiO}_2$  in the flux maintained good fluidity even with substantial consumption of FeO, proving its efficacy as an excellent dephosphorization flux [8,11].

## 5.2. Mineral Phases of Composite Calcium Ferrite Slag

The micro-morphology and chemical composition of the dephosphorization final slag in the CF and CAF flux-containing slag systems are displayed in Figure 7 and Table 6. SEM-EDS comparative analysis of the final slag phases showed that the CF slag system primarily consisted of unreacted lime particles, dicalcium silicate (C2S), minor calcium ferrite (CF), and solid solution  $2\text{CaO}\cdot\text{SiO}_2\text{--}3\text{CaO}\cdot\text{P}_2\text{O}_5$  (C2S–C3P). The CAF slag system distinctly featured an amorphous matrix phase (gray), iron-bearing matrix phase (white), and oval-shaped phosphorus-enriched phase (dark gray). Combined with XRD phase analysis from Figure 7 for the CAF slag system, the amorphous matrix phase was mainly a low-melting liquid slag phase, the iron-bearing matrix phase was primarily iron aluminate spinel, and the phosphorus-enriched phase existed in the forms of C2S–C3P or nC2S–C3P and Na-rich phosphorus phase  $\text{Na}_2\text{C}_2\text{P}$ . Further high-resolution SEM analysis of local slag phases revealed that the phosphorus-enriched phase was concentrated inside the oval shapes, coinciding with the enrichment of elements like Ca, Si, and Na. Particularly, the Na element was enriched around the P element, consistent with the Ca distribution but differing from Si, also proving the formation of the Na-rich phosphorus phase. Compared

to the phosphorus-enriched phase area ratio in both slag systems, the proportion in the CAF slag system was higher than in the CF system, with the highest phosphorus content in the solid solution reaching 17.71 wt% (Table 6).

The addition of CAF flux containing  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{Na}_2\text{O}$  also impacted phosphorus enrichment. Studies indicated [9] that  $\text{Al}_2\text{O}_3$  could increase the phosphorus content in the C2S-C3P solid solution but also increase the liquid slag phase. When  $\text{Na}_2\text{O}$  replaced  $\text{CaO}$ , it could transform from C2S-C3P to C2S-N2C2P, releasing  $\text{CaO}$ , which then combined to form new C2S, thereby increasing the overall solid solution content in the slag. Hence, under the combined interactions, a phosphorus-enriched phase with a high phosphorus concentration was obtained [8,11].

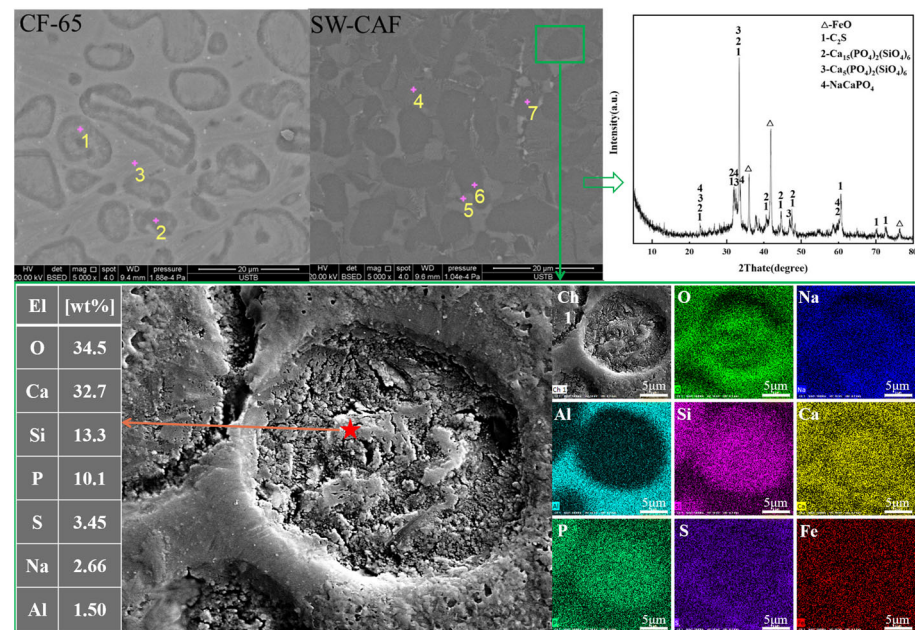


**Figure 7.** The SEM patterns of CF-65 and SW-CAF final slag, and the XRD pattern of SW-CAF. 1–7 refers to the EDS component information at the corresponding position in the figure. As shown in Table 6.

**Table 6.** The EDS energy spectrum analysis of each point (wt%).

| Point | Ca    | Si    | P     | S    | Na   | Fe   | Al    | Ti    | Mn   |
|-------|-------|-------|-------|------|------|------|-------|-------|------|
| 1     | 34.62 |       |       |      |      |      |       |       |      |
| 2     | 40.1  | 12.23 |       |      |      | 6.02 |       |       |      |
| 3     | 64.22 | 22.8  | 3.92  | 1.5  |      |      |       |       | 4.57 |
| 4     | 28.94 | 5.36  | 2.73  | 1.85 | 0.27 | 5.74 | 13.85 | 0.25  | 5.24 |
| 5     | 28.78 | 3.48  | 3.79  | 1.66 | 1.06 |      | 3.77  | 12.97 |      |
| 6     | 57.9  | 13.47 | 17.71 | 4.19 | 1.72 |      |       | 6.74  |      |
| 7     | 27.72 | 11.43 | 9.12  | 1.87 |      | 2.8  | 7.06  |       | 3.51 |

### 5.3. Utilization Rate of Lime

The utilization rate of lime reflects the performance of the flux. Research by Shiro [5] showed that when [Si] and [Mn] in hot metal are in trace amounts, a dephosphorization agent with over 50% iron oxide content has sufficient oxidizing capability. Therefore, the dephosphorization ability depends on the supply of  $\text{CaO}$ . In this experiment, the theoretical impact of [Si] and [Mn] in hot metal on the demand for oxidizers was considered. With an iron oxide content above 60% being sufficient, it is still possible to compare the dephosphorization abilities of fluxes using Equation (1).

$$\Delta n_{\text{P}}/n_{\text{CaO}} = (n_{\text{P}0} - n_{\text{P}t})/n_{\text{CaO}} \quad (1)$$

$n_{P0}$ : the initial molar number of [P] in hot metal (mol);  $n_{Pt}$ : the molar number of [P] in hot metal at  $t$  minutes (mol);  $n_{CaO}$ : the number of moles of CaO added at  $t$  minutes (mol).  $\Delta n_P/n_{CaO}$  is defined as the CaO utilization efficiency during hot metal treatment.

Figure 8 shows the CaO utilization efficiency in high-phosphorus iron dephosphorization experiments H1 to H3, regular iron dephosphorization experiments L1 to L3, and induction furnace experiment G3. It was observed that under the same [%P] conditions in hot metal, the lime utilization efficiency was highest in the slag system containing CAF flux and lowest in the  $CaO+Fe_2O_3$  slag system. Compared to high-phosphorus iron, regular iron generally had a lower lime utilization rate during dephosphorization, even lower than the  $CaO+Fe_2O_3$  slag system in high-phosphorus iron. The lime utilization efficiency in the group containing CAF flux (including kilogram-scale expanded experiments) increased over time, while it remained relatively unchanged over time in the group containing CF flux. It was foreseeable that with the increase in reaction time, the advantages of CAF would become more apparent. Comparing the results of this study with Shiro's research [5], the  $CaO-Fe_2O_3$  slag system had similar lime utilization efficiency to CF in this study, while the  $CaO-Fe_2O_3-Al_2O_3$  slag system's efficiency was closer to this study's  $Al_2O_3/Na_2O/TiO_2$  composite calcium ferrite flux. Since there was no silicon in the hot metal, and no  $SiO_2$  in the slag, the dissolved lime was primarily used for dephosphorization. In this study, lime was used not only for dephosphorization but also in the formation of calcium silicate, explaining its relatively lower utilization rate. In summary, CAF prepared from solid waste exhibited high efficiency in the pre-dephosphorization of hot metal. This flux not only significantly reduced raw material costs but also enhanced the utilization efficiency of lime, potentially bringing transformative breakthroughs in the pre-treatment phase of hot metal or early converter steelmaking.

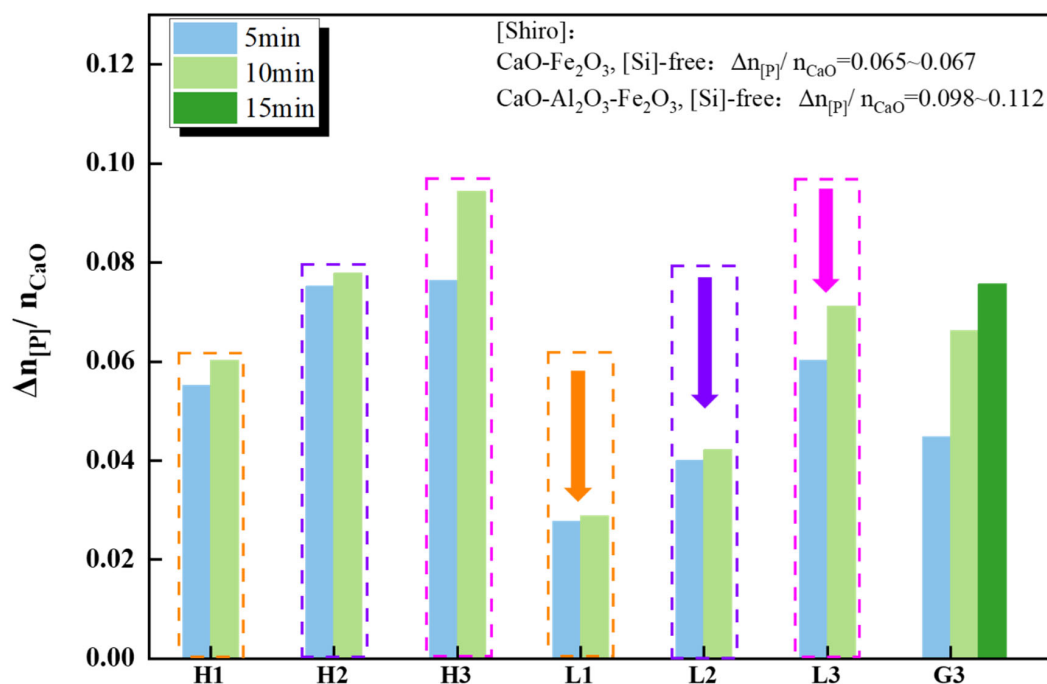


**Figure 8.** Lime utilization efficiency. Dashed lines of the same color represent comparisons of values using the same melt group. The arrows point to a decreasing trend in values between the same groups.

## 6. Conclusions

This study, utilizing industrial solid waste red mud, successfully developed a novel low-melting-point flux SW-CAF. The melting characteristics of SW-CAF were explored, and high-temperature dephosphorization experiments were conducted. By comparing the dephosphorization effects of different fluxes, SW-CAF demonstrated excellent lime

dissolution and good fluidity, offering significant advantages in the pre-dephosphorization process of hot metal. The specific results are as follows:

- (1) The primary phases of the low-melting-point dephosphorization flux were  $\text{CaFe}_2\text{O}_4$ ,  $\text{Ca}_2\text{Fe}_2\text{O}_4$ , and  $\text{Ca}_2(\text{Fe,Al})_2\text{O}_4$ , collectively termed composite calcium ferrite. The complete melting temperature of this flux was about 1186 °C, with the beneficial dephosphorization components ( $\text{Fe}_2\text{O}_3 + \text{CaO}$ ) exceeding 80%, offering significant advantages such as a high iron oxide content, high alkalinity, a low melting point, and good melting fluidity.
- (2) Simulating the dephosphorization process of hot metal using high-phosphorus ore ([%P] = 0.25 wt%) and regular iron ([%P] = 0.14 wt%), composite calcium ferrite exhibited superior dephosphorization effectiveness compared to synthetic calcium ferrite. With a high carbon content ([%C] = 3.2 wt%), a dephosphorization rate above 90% and a final [%P] content below 0.02 wt% were achieved. Regardless of the initial phosphorus content and the quantity of hot metal (200 g and kilogram-scale), excellent dephosphorization results were replicated using composite calcium ferrite.
- (3) In the dephosphorization slag with added composite calcium ferrite flux, the phosphorus-enriched phase was primarily nC2S-C3P solid solution, with a minor presence of  $\text{Na}_2\text{O}$ -containing N2C2P solid solution. The highest phosphorus content in the solid solution reached 17.71 wt%, significantly exceeding the 3.92 wt% in CF slag.
- (4) In the pre-dephosphorization of hot metal, using composite calcium ferrite flux enabled efficient lime melting and rapid slag formation even at lower temperatures. Compared to CF flux, the slag melting time increased by 50% and by 70% compared to the conventional  $\text{CaO} + \text{Fe}_2\text{O}_3$  slag system. During dephosphorization, composite calcium ferrite enhanced lime utilization efficiency, extended the re-drying period, and achieved a high dephosphorization rate with lower carbon loss, significantly surpassing CF flux.
- (5) At the conclusion of the steelmaking process, the application of composite calcium ferrite flux was observed to facilitate effective slag–metal separation. This is critically significant for the removal of high-phosphorus slag and ensuring efficient slag–steel separation during the final phases of steelmaking.

Consequently, the composite calcium ferrite derived from solid waste is expected to be a superior fluorine-free flux for steelmaking. This innovative material is positioned to play a crucial role in the manufacturing of high-end steel grades with low or ultra-low phosphorus content.

**Author Contributions:** Conceptualization, Z.Z. and Y.Z. (Yanling Zhang); methodology, Z.Z. and X.F.; formal analysis, Z.Z.; investigation, Z.Z. and Y.Z. (Yao Zhang); writing—original draft preparation, Z.Z.; writing—review and editing, Z.Z. and Y.Z. (Yanling Zhang); visualization, Y.Z. (Yao Zhang) and Y.W.; supervision, X.F. and Y.Z. (Yanling Zhang). All authors have read and agreed to the published version of the manuscript.

**Funding:** We would like to thank the National Natural Science Foundation of China (U1960201) and the National Key R&D Program of China (2019YFC1905701) for the financial support.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Conflicts of Interest:** Author Xiaoming Feng was employed by the company Jianlong Steel Holdings Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

## References

1. Wu, W.; Yang, Q.; GAO, Q.; Zeng, J. Effects of Calcium Ferrite Slag on Dephosphorization of Hot Metal during Pretreatment in the BOF Converter. *J. Mater. Res. Technol.* **2020**, *9*, 2754–2761. [[CrossRef](#)]
2. Du, C.; Gao, X.; Kitamura, S. Measures to Decrease and Utilize Steelmaking Slag. *J. Sustain. Metall.* **2019**, *5*, 141–153. [[CrossRef](#)]

3. Sato, T.; Nakashima, K.; Mori, K. Dephosphorization Rate of High Carbon Iron Melts by CaO-Based Slags. *Tetsu Hagané* **2001**, *87*, 643–649. [CrossRef] [PubMed]
4. Li, F. Study on Basic Properties and Dephosphorization Behavior of Steelmaking Slag Based on Red Mud Based Flux. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2019.
5. Ban-Ya, S.; Hino, M.; Nagabayashi, R.; Terayama, O. Dephosphorization and Desulphurization of Hot Metal with CaO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> Flux. *Tetsu Hagané* **1989**, *75*, 66–73. [CrossRef] [PubMed]
6. Zhang, M.; Li, J.; Jia, C.; Yu, Y. Dissolution Behavior of Lime with Different Properties into Converter Slag. *Materials* **2023**, *16*, 6487. [CrossRef]
7. Jeong, T.S.; Park, J.H. Effect of Fluorspar and Industrial Wastes (Red Mud and Ferromanganese Slag) on Desulfurization Efficiency of Molten Steel. *Metall. Mater. Trans. B* **2020**, *51*, 2309–2320. [CrossRef]
8. Jiang, L.; Diao, J.; Yan, X.; Xie, B.; Ren, Y.; Zhang, T.; Fan, G. Effect of Al<sub>2</sub>O<sub>3</sub> on Enrichment of Phosphorus in Hot Metal Dephosphorization Slag. *ISIJ Int.* **2015**, *55*, 564–569. [CrossRef]
9. Du, C.; Gao, X.; Ueda, S.; Kitamura, S. Distribution of P<sub>2</sub>O<sub>5</sub> and Na<sub>2</sub>O Between Solid Solution and Liquid Phase in the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-Na<sub>2</sub>O Slag System with High P<sub>2</sub>O<sub>5</sub> Content. *Metall. Mater. Trans. B* **2018**, *49*, 181–189. [CrossRef]
10. Li, F.; Zhang, Y.; Guo, Z. Pilot-Scale Test of Dephosphorization in Steelmaking Using Red Mud-Based Flux. *JOM* **2017**, *69*, 1624–1631. [CrossRef]
11. Zhang, Y.; Li, F.; Yu, K. Using Red Mud-Based Flux in Steelmaking for High Phosphorus Hot Metal. *ISIJ Int.* **2018**, *58*, 2153–2155. [CrossRef]
12. Jeon, J.-W.; Jung, S.-M.; Sasaki, Y. Formation of Calcium Ferrites under Controlled Oxygen Potentials at 1273 K. *ISIJ Int.* **2010**, *50*, 1064–1070. [CrossRef]
13. Lee, M.S.; Barr, P.V. Production and Properties of Burnt Lime Coated with Dicalcium Ferrite. *Ironmak. Steelmak.* **2002**, *29*, 96–100. [CrossRef]
14. Wu, W.; Zhao, B.; Zhao, B.; Wu, W.; Meng, H. Hot Metal Dephosphorization Process Using Calcium Ferrite Slag without Fluorite. *Ironmak. Steelmak.* **2022**, *49*, 661–668. [CrossRef]
15. Sukenaga, S.; Gonda, Y.; Yoshimura, S.; Saito, N.; Nakashima, K. Viscosity Measurement of Calcium Ferrite Based Slags during Structural Relaxation Process. *ISIJ Int.* **2010**, *50*, 195–199. [CrossRef]
16. Lee, W.-G.; Song, M.-S. CO<sub>2</sub> Adsorption Reactions of Synthetic Calcium Aluminum Ferrite (CAF). *Appl. Sci.* **2022**, *12*, 6677. [CrossRef]
17. Mi, G.; Murakami, Y.; Shindo, D.; Saito, F.; Shimme, K.; Masuda, S. Mechanochemical Synthesis of Calcium Ferrite by a Planetary Mill and Its Dephosphorization Characteristic from Molten Iron. *J. Min. Mater. Process. Inst. Jpn.* **1999**, *115*, 683–688.
18. Karamoutsos, S.; Tzeveleku, T.; Christogerou, A.; Grilla, E.; Gypakis, A.; Villarejo, L.P.; Mantzavinos, D.; Angelopoulos, G.N. On the Industrial Symbiosis of Alumina and Iron/Steel Production: Suitability of Ferroalumina as Raw Material in Iron and Steel Making. *Waste Manag. Res.* **2021**, *39*, 1270–1276. [CrossRef] [PubMed]
19. Sun, J.; Liu, C.; Jiang, M. Design of Red Mud-Based Desiliconization and Dephosphorization Flux and Its Application in Ferromanganese. *ISIJ Int.* **2021**, *61*, 1835–1841. [CrossRef]
20. Bang, K.-H.; Kang, Y.-B. Recycling Red Mud to Develop a Competitive Desulfurization Flux for Kanbara Reactor (KR) Desulfurization Process. *J. Hazard. Mater.* **2022**, *440*, 129752. [CrossRef]
21. Ning, G.; Zhang, B.; Liu, C.; Li, S.; Ye, Y.; Jiang, M. Large-Scale Consumption and Zero-Waste Recycling Method of Red Mud in Steel Making Process. *Minerals* **2018**, *8*, 102. [CrossRef]
22. Dmitriev, A. The Comprehensive Utilisation of Red Mud Utilisation in Blast Furnace. In *Recovery and Utilization of Metallurgical Solid Waste*; Zhang, Y., Ed.; IntechOpen: Rijeka, Croatia, 2018; Available online: <https://www.intechopen.com/books/recovery-and-utilization-of-metallurgical-solid-waste/the-comprehensive-utilisation-of-red-mud-utilisation-in-blast-furnace> (accessed on 20 February 2019).
23. Trushko, V.L.; Utkov, V.A.; Sivushov, A.A. Reducing the Environmental Impact of Blast Furnaces by Means of Red Mud from Alumina Production. *Steel Transl.* **2017**, *47*, 576–578. [CrossRef]
24. Zhao, J.; Su, H.; Zuo, H.; Wang, J.; Xue, Q. The Mechanism of Preparation Calcium Ferrite from Desulfurization Gypsum Produced in Sintering. *J. Clean. Prod.* **2020**, *267*, 122002. [CrossRef]
25. Kim, D.-G.; Van Ende, M.-A.; van Hoek, C.; Liebske, C.; van der Laan, S.; Jung, I.-H. A Critical Evaluation and Thermodynamic Optimization of the CaO-CaF<sub>2</sub> System. *Metall. Mater. Trans. B* **2012**, *43*, 1315–1325. [CrossRef]
26. Katahira, Y.; Hayashi, M. Activities of FeO<sub>1.33</sub> in the FeO<sub>x</sub>-CaO-SiO<sub>2</sub> and FeO<sub>x</sub>-CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Slags at 1573 K Under Oxygen Partial Pressures between 10<sup>-6</sup> and 10<sup>-2</sup> atm. *ISIJ Int.* **2016**, *56*, 1164–1170. [CrossRef]
27. Yang, M.; Lv, X.; Wei, R.; Bai, C. Wetting Behavior of TiO<sub>2</sub> by Calcium Ferrite Slag at 1523 K. *Metall. Mater. Trans. B* **2018**, *49*, 2667–2680. [CrossRef]
28. Kawanishi, S.; Shibata, H.; Yoshikawa, T. Contribution of Dislocations in SiC Seed Crystals on the Melt-Back Process in SiC Solution Growth. *Materials* **2022**, *15*, 1796. [CrossRef]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.