

Article

Modification of Copper Slag Using Steel Slag and Magnesium Slag Additives

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Abstract

Significant amounts of smelting slag are generated during the production of steel, refined copper, and refined magnesium. These slags contain abundant valuable metallic elements, such as Fe, Cu, Zn, Co, and Mg, that have not been fully utilized in the past. This study proposes a method for modifying copper slag by mixing it with steel slag and magnesium slag, followed by roasting with additions of Fe₂O₃ and MgO. The samples were roasted at 1400 °C for 30 min, cooled to 1000 °C at 1.5 °C/min, and then water-quenched to room temperature. Phase transformations during modification were analyzed using FactSage 8.0, DSC–TG, and XRD. The effects of factors such as the content of Fe₂O₃ and MgO on the modification efficiency were investigated. The results indicate that, under the condition of maintaining a steel slag: copper slag: magnesium slag ratio of 37:37:26 and adjusting the basicity (CaO/SiO₂ ratio) with CaO to 2.0, the addition of Fe₂O₃ and MgO promotes the formation of spinel. However, excessively high contents of Fe₂O₃ and MgO lead to refinement of the spinel grains and reduce the iron grade of the concentrate. Within the investigated composition range, the samples with total Fe₂O₃ and MgO contents of 27.66 wt% and 7.56 wt%, respectively, showed the best magnetic separation performance among the tested compositions. Through magnetic separation, the concentrate has good economic and industrial application value in industries such as steelmaking and powder metallurgy, while the tailings can be utilized as raw materials for manufacturing ceramics, glass–ceramics, cement, and concrete.

Keywords: copper slag; magnesium slag; composite modification; spinel

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1. Introduction

With the continuous advancement of global industrialization, the large-scale accumulation of smelting slags has become a significant bottleneck restricting sustainable resource utilization and ecological preservation [1]. In China, for instance, the annual production of steel slag has exceeded 100 million tons, with a cumulative stockpile reaching over 1.9 billion tons [2]. Simultaneously, the pyrometallurgical copper smelting process generates vast quantities of copper slag; for every ton of refined copper produced, approximately 2 to 3 tons of copper slag are generated, leading to a global annual output exceeding 70 million tons [3]. Furthermore, as the world's largest magnesium producer,

China generates over 5 tons of magnesium slag for every ton of refined magnesium produced via the Pidgeon process [4]. Currently, the majority of these slags are managed through surface stockpiling or landfilling. These practices not only consume extensive land resources but also allow heavy metals to permeate into the soil, resulting in severe environmental degradation and posing risks to atmospheric quality and human health.

The primary chemical components of steel slag include CaO , SiO_2 , Al_2O_3 , Fe_xO , and MgO , with the mineral phases predominantly existing as silicates. Notably, steel slag contains a relatively high iron content (approximately 10–20 wt%), presenting significant recovery value [2]. Research by Zhu et al. [5] demonstrated that grinding aids can increase the specific surface area of steel slag, thereby accelerating its early-stage hydration; furthermore, composite steel slag can enhance overall reactivity. This can effectively improve the performance of building materials. Zheng et al. [6] investigated the factors influencing the activity of steel slag using steel slag and silica fume as raw materials, finding that the addition of silica fume and blast furnace slag can effectively stimulate the pozzolanic activity of the steel slag. Fang et al. [7] utilized steel slag and fly ash as partial cement replacements, noting that moderate steel slag addition improves the compressive strength and cementitious properties, while fly ash enhances long-term strength. Despite existing attempts to utilize smelting slags in cement production, concrete admixtures, agricultural fertilizers, or wastewater treatment, most methods fail to fully exploit the slag's potential or result in secondary waste that is difficult to manage [2], hindering large-scale industrial adoption. Crucially, given China's high demand and heavy import reliance on iron ore, recovering iron from steel slag could significantly alleviate the economic pressure of high-cost ore imports on the steel industry [2].

The mineralogical composition of copper slag primarily consists of SiO_2 , CaO , Fe_xO , and minor amounts of metallic elements in free form. Copper slag is rich in silicon and iron; silicon exists mainly in silicate forms, while iron is primarily hosted in fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4) [8]. Since fayalite is weakly magnetic, conventional magnetic separation is ineffective for iron recovery [9]. Qu et al. [10] achieved the recovery of copper and iron through a combined reduction-magnetic separation process, while manganese in the tailings was recovered via acid leaching. Li et al. [11] employed a reduction-sulfidation method at 1350 °C to extract copper, cobalt, and other metals. Zhang et al. [12] utilized sulfuric acid leaching while suppressing the interference of iron oxides and silica, achieving leaching rates of 89%, 98%, and 97% for Cu, Co, and Zn, respectively. Shi et al. [13] proposed a high-pressure oxidative acid leaching technique to recover valuable metals, facilitating the transformation of iron phases into hematite. However, these methods generally fail to efficiently recover the bulk iron content, representing a substantial waste of resources.

Magnesium slag is mainly composed of CaO , SiO_2 , Al_2O_3 , Fe_xO , and MgO . Most magnesium slags are basic slags, with a basicity ratio (CaO/SiO_2) generally exceeding 1.5 [11]. Peng et al. [14] replaced cement clinker with two types of magnesium slag to prepare Portland cement; their findings indicated that magnesium slag addition extends the setting time of the cement. Currently, some Chinese magnesium producers employ the back-filling method for slag disposal, although this method is relatively efficient and environmentally friendly, making it prohibitively expensive [11]. Consequently, many small-scale enterprises are unable to adopt this method or effectively utilize the high-activity CaO present in the slag. The treatment of these high-alkalinity wastes remains costly, necessitating the urgent development of more efficient and economical utilization strategies [1].

To address these challenges, this study proposes a “waste-to-waste” synergistic modification pathway for multi-component metallurgical slags. The core logic involves leveraging the “component compensation” effect between steel, copper, and magnesium slags; the high iron content in copper slag compensates for the lower iron grade in steel slag,

while the calcium and magnesium in magnesium slag regulate the alkalinity of the system [15]. During high-temperature roasting, this synergistic effect drives the phase transformation of weakly magnetic fayalite into a strongly magnetic spinel solid solution (magnetioferrite spinel, $(\text{Mg}, \text{Fe})\text{Fe}_2\text{O}_4$), thereby enhancing iron recovery [9]. Furthermore, the incorporation of free CaO and MgO into the silicate phase mitigates expansion issues and improves the reactivity of the tailings for use as raw materials in construction [16].

In this work, thermodynamic simulations were conducted using FactSage 8.0, supplemented by SEM, EDS, and XRD analysis, to systematically investigate the influence of Fe_2O_3 and MgO levels (adjusted via slag proportioning) on phase evolution. By elucidating the modification mechanisms, this study aims to identify preferred component ranges within the tested compositions that allow the magnetic concentrate to be utilized in iron-making-related applications, while the tailings are repurposed for high-value applications such as ceramics, glass–ceramics, and cement. This research provides a theoretical foundation for the one-step synergistic consumption of bulk industrial solid wastes and offers new insights into phase transformation control within complex slag systems.

2. Materials and Methods

2.1. Thermodynamic Feasibility Analysis

According to Figure 1, increasing Fe_2O_3 content lowers the liquidus temperature and also leads to the formation of unstable calcium monoferrite (CaFe_2O_4) in the temperature range of 1100–1200 °C. At higher Fe_2O_3 contents, residual Fe_2O_3 remains in the low-temperature region around 1100 °C. This residual Fe_2O_3 is excessively oxidized to Fe_3O_4 in the high-temperature region as the temperature increases. Under all Fe_2O_3 content conditions, a transformation occurs at 1400 °C where α' - Ca_2SiO_4 transforms to α - Ca_2SiO_4 . At lower Fe_2O_3 contents, iron-magnesium monoxide ($\text{Fe}, \text{Mg})\text{O}$ precipitates at 1400 °C. As Fe_2O_3 content increases, at 1400 °C, these iron-magnesium monoxides transform to kirschsteinite (CaFeSiO_4), which is unfavorable for spinel nucleation in the high-temperature region.

Figure 2 shows that as MgO content increases, the region-forming spinel does not expand; instead, the region-forming kirschsteinite increases. Excess iron not only combines with CaO and SiO_2 to form kirschsteinite, but also, when MgO content exceeds 9.2%, free iron monoxide exists in the low-temperature region. Excessively high MgO content inhibits the formation of α' - Ca_2SiO_4 and raises its formation temperature. Increasing MgO content slightly raises the liquidus temperature while lowering the precipitation temperature of iron-magnesium monoxides. At any MgO content, an α' - $\text{Ca}_2\text{SiO}_4/\alpha$ - Ca_2SiO_4 transformation line exists at 1400 °C, accompanied by precipitation of iron-magnesium monoxides. These oxides can create conditions for heterogeneous nucleation of spinel, promoting its formation. Excessively high MgO can cause the silicate phase to disappear, resulting in tailings after magnetic separation lacking Ca_2SiO_4 and making them unsuitable for direct use in building materials. Therefore, under the present experimental conditions, the total MgO content should be controlled within a relatively low range. In the M-series samples investigated in this study, the total MgO content ranged from 5.71 to 11.05 wt%, and contents above 9.34 wt% tended to promote merwinite/amorphous phases and spinel refinement.

Figure 3 indicates that as Fe_2O_3 content increases, the content of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) decreases, while that of monocalcium ferrite (CaFe_2O_4) increases. The phase content of α' - Ca_2SiO_4 slightly decreases, and the spinel phase content shows no significant change. Excess Fe_2O_3 does not generate substantial spinel in the medium-temperature range; instead, it combines with free CaO to form calcium ferrites. Increasing Fe_2O_3 content also leads to earlier precipitation of the liquid phase. Meanwhile, the iron-magnesium monoxides, which are precipitated in the high-temperature region, gradually dissolve and disappear, and kirschsteinite also progressively dissolves. Increasing Fe_2O_3 content inhib-

its the formation of the α -Ca₂SiO₄ phase, causing α -Ca₂SiO₄ to transform into the liquid phase at high temperatures, promoting spinel formation. In sample F4 with the highest Fe₂O₃ content, residual unreacted Fe₂O₃ remains in the low-temperature region. This Fe₂O₃ undergoes excessive oxidation as temperature rises, transforming into dicalcium ferrite and spinel. Therefore, during roasting, the iron content in the smelting slag should be controlled. An appropriate iron content can promote the formation of spinel and silicate phases while inhibiting calcium ferrite formation. However, an excessively high iron grade reduces the yield of spinel and silicate phases and increases calcium ferrites.

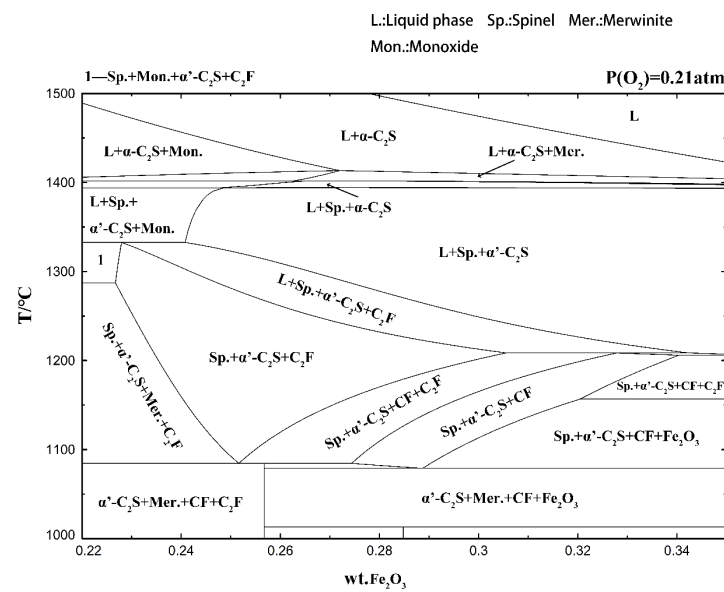


Figure 1. Thermodynamic diagram (different Fe₂O₃ contents).

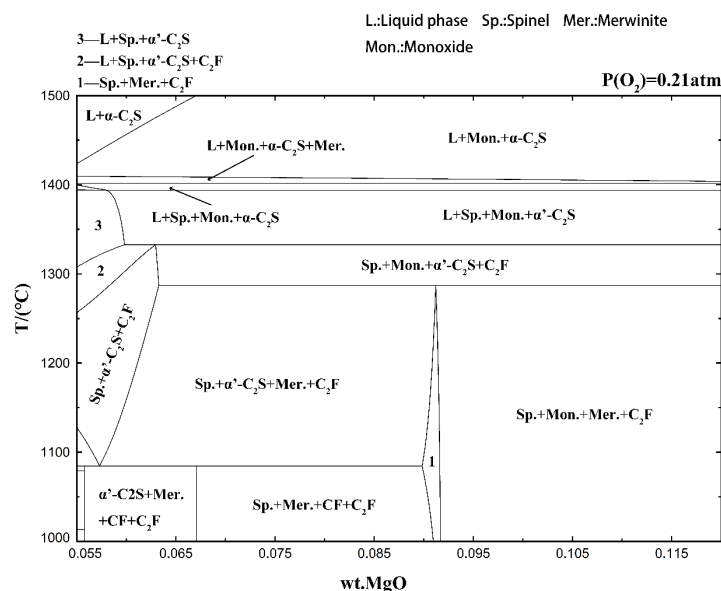


Figure 2. Thermodynamic diagram (different MgO contents).

Figure 4 shows that as MgO content increases, the content of merwinite (Ca₃Mg(SiO₄)₂) gradually increases. Iron-magnesium monoxides appear and increase at lower temperatures with increasing MgO content. This phenomenon lowers the formation temperature of α' -Ca₂SiO₄ and reduces its content; thus, excessively high MgO does not promote silicate phase formation. Increasing MgO content also increases dicalcium ferrite content, reducing the activity of the tailings. Increasing MgO content also reduces spinel

content and significantly lowers its formation temperature. At higher MgO contents, MgO, CaO, and SiO₂ in the mixed slag can form the stable mineral phase merwinite (Ca₃Mg(SiO₄)₂). This phase consumes substantial SiO₂ and CaO from the mixed slag, preventing stable formation of the Ca₂SiO₄ phase at lower temperatures. Simultaneously, merwinite formation increases the local Ca/Fe ratio, leading to the production of large amounts of dicalcium ferrite and inhibiting spinel generation. Therefore, MgO content must be strictly controlled to promote spinel formation while reducing the generation of merwinite and calcium ferrites.

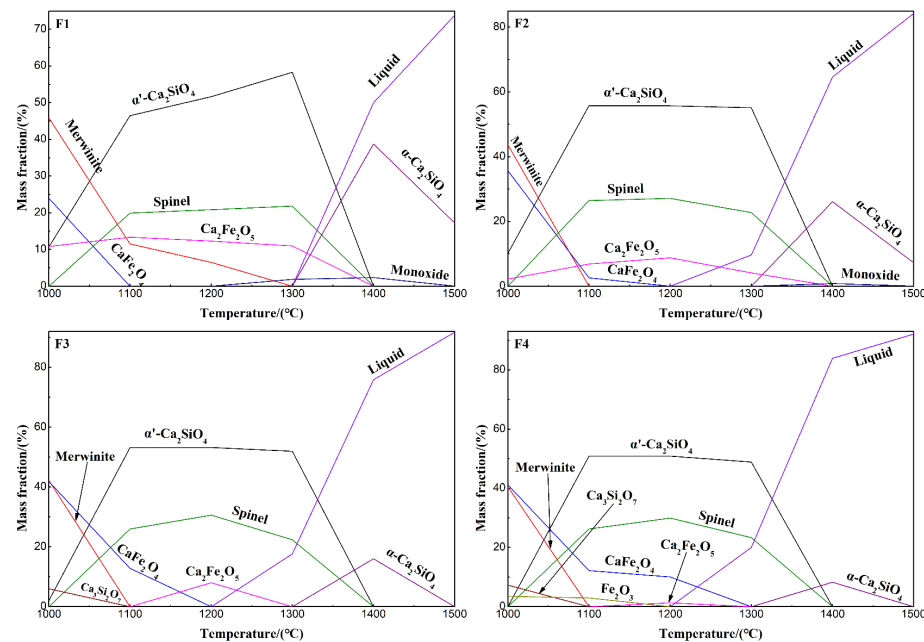


Figure 3. Equilibrium diagram (different Fe₂O₃ contents): (F1) sample with 24.06 wt% total Fe₂O₃. (F2) sample with 27.66 wt% total Fe₂O₃. (F3) sample with 30.97 wt% total Fe₂O₃. (F4) sample with 33.96 wt% total Fe₂O₃.

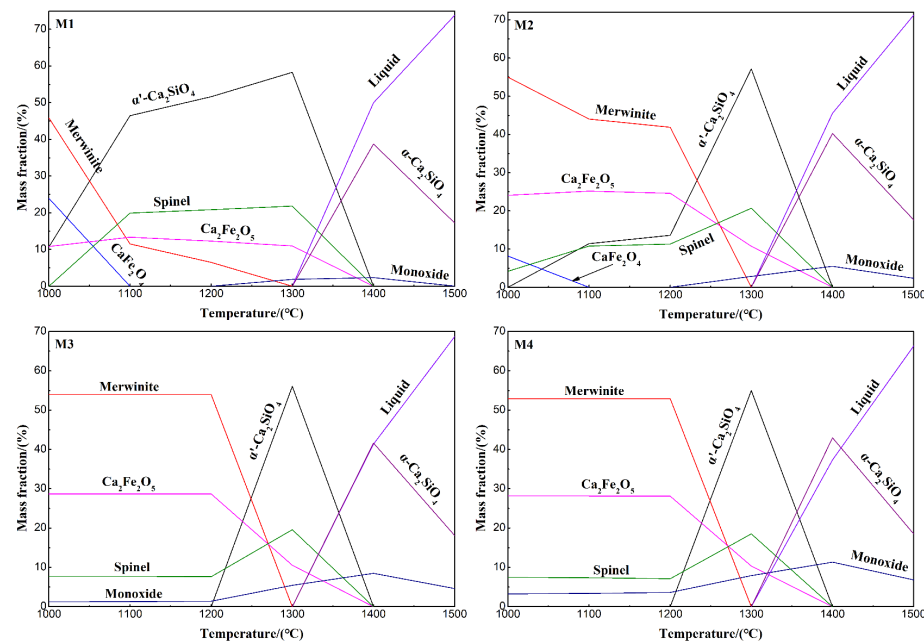


Figure 4. Equilibrium diagram (different MgO contents): (M1) sample with 5.71 wt% total MgO. (M2) sample with 7.56 wt% total MgO. (M3) sample with 9.34 wt% total MgO. (M4) sample with 11.05 wt% total MgO.

2.2. Materials

The materials used in the experiment were steel slag (from a domestic steel smelting enterprise), copper slag (from a domestic copper smelting enterprise), magnesium slag (from a domestic magnesium smelting enterprise), CaO (Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China), Fe₂O₃ (Shanghai Macklin Biochemical Technology Co., Ltd.), and MgO (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Table 1 and Figures 5–7 show the chemical and phase compositions of the three raw slags. Iron in the steel slag exists mainly as magnetite (Fe₃O₄) and fayalite (Fe₂SiO₄), while magnesium exists mainly as forsterite (Mg₂SiO₄). Iron in the copper slag also mainly exists as fayalite, which is weakly magnetic and difficult to recover by direct magnetic separation. Magnesium slag contains more than 50 wt% CaO and provides CaO/MgO components for basicity adjustment and spinel formation. Based on the compositional complementarity of the three slags and preliminary basicity optimization, steel slag, copper slag, and magnesium slag were mixed at a mass ratio of 37:37:26. In this mixture, copper slag provides Fe-bearing fayalite, steel slag contributes additional iron-bearing phases, and magnesium slag supplies CaO/MgO. Additional CaO was then added to adjust the basicity (CaO/SiO₂ ratio) to 2.0. The original slag compositions are listed in Table 1, whereas Table 2 shows the calculated compositions of the mixed slags after blending and reagent addition. The F-series samples (F1–F4) were designed to examine the effect of increasing total Fe₂O₃ content, while the M-series samples (M1–M4) were designed to examine the effect of increasing total MgO content. F1 and M1 are the baseline compositions without additional Fe₂O₃ or MgO.

Table 1. Chemical composition of the raw materials.

Slag	Components (wt%)						
	MgO	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	Cu ₂ S	Others
SS	13.48	21.50	34.81	21.78	4.49	0	3.94
CS	1.19	31.29	1.64	54.08	4.87	3.01	3.92
MS	12.62	20.69	57.09	4.50	0	0	5.10

Table 2. Calculated compositions of mixed slags after blending and reagent addition.

Num.	Components (wt%)								
	MgO	SiO ₂	CaO	Fe ₂ O ₃	Additional CaO	Additional Fe ₂ O ₃	Additional MgO	Total Fe ₂ O ₃	Total MgO
F1	5.71	20.50	23.32	24.06	17.69	0	0	24.06	5.71
F2	5.44	19.53	21.21	22.92	16.85	4.74	0	27.66	5.44
F3	5.19	18.64	21.20	21.88	16.08	9.09	0	30.97	5.19
F4	5.00	17.83	20.28	20.92	15.38	13.04	0	33.96	5.00
M1	5.71	20.50	23.32	24.06	17.69	0	0	24.06	5.71
M2	5.60	20.10	22.86	23.59	17.34	0	1.96	23.59	7.56
M3	5.49	19.72	22.42	23.14	17.01	0	3.85	23.14	9.34
M4	5.39	19.34	22.00	22.70	16.69	0	5.66	22.70	11.05

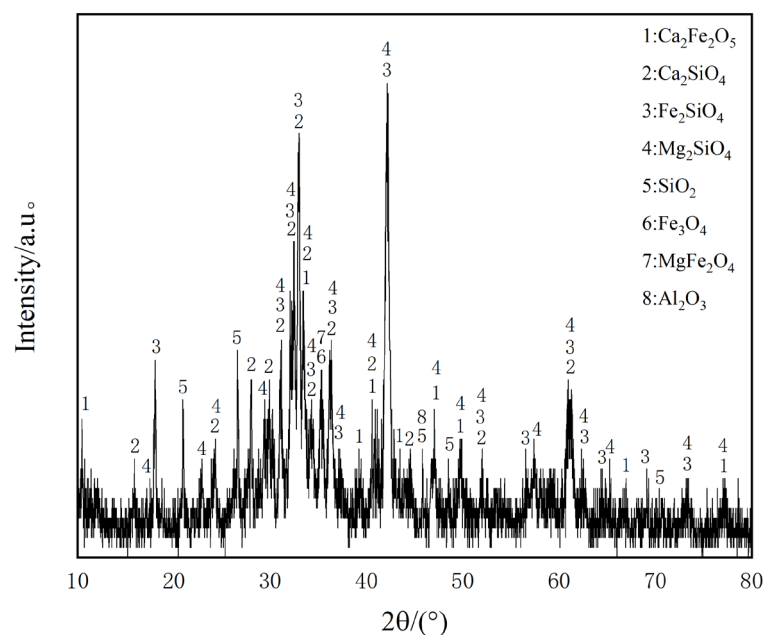


Figure 5. XRD patterns (SS).

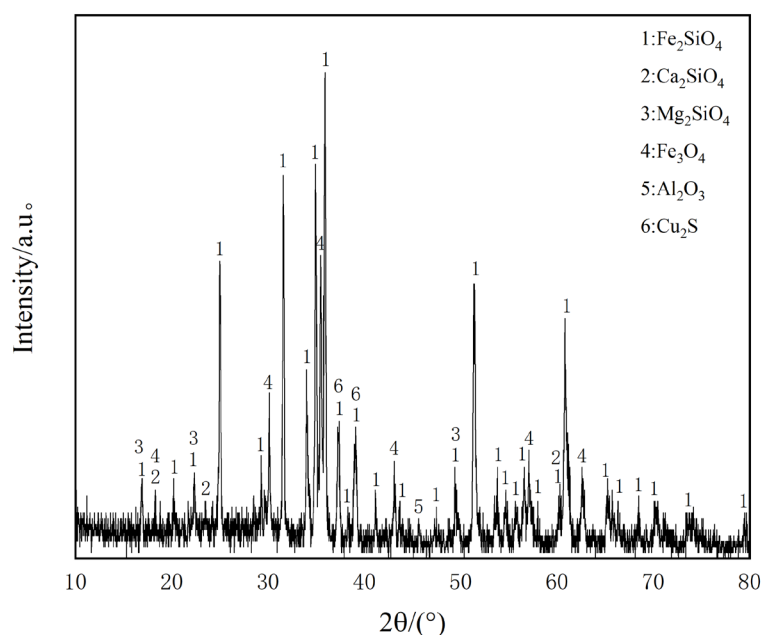


Figure 6. XRD patterns (CS).

2.3. Methods

2.3.1. Process Flow

In this experiment, raw materials were mixed and heated to a molten state to simulate actual industrial slagging conditions. First, predetermined proportions of steel slag, copper slag, and magnesium slag were mixed with specific amounts of CaO, Fe₂O₃, and MgO. These materials were then mixed using a mixer for 6 h, pressed into small pellets using a press, put into MgO crucible, and placed in a muffle furnace for roasting. The roasting atmosphere was air, and the temperature was 1400 °C. After holding at 1400 °C for 30 min, the temperature was lowered to 1000 °C at a cooling rate of 1.5 °C/min, followed by water quenching to room temperature. This roasting–cooling schedule was used for all F-series and M-series samples unless otherwise stated. Phase analysis was performed on the roasted samples. Finally, the samples were placed in a wet magnetic separation solenoid

for separation of the spinel and silicate phases at a magnetic field intensity of 250 A/m. The iron grade of the concentrate after magnetic separation was determined according to the Chinese National Standard GB/T 6730.65-2009 “Iron ores[17]—Determination of total iron content—Titanium trichloride reduction potassium dichromate titrimetric method (routine method),” and the iron recovery rate was calculated [17].

$$\beta = M_1/M_2 \times 100\% \quad (1)$$

$$N = M_3/M_4 \times 100\% \quad (2)$$

$$P = M_3/M_5 \times 100\% \quad (3)$$

where β is magnetic separation yield, N is iron grade, P is iron recovery rate, M_1 is concentrate mass, M_2 is total mass of mixed slag, M_3 is total iron content in concentrate, M_4 is total mass of concentrate, and M_5 is total iron content in mixed slag.

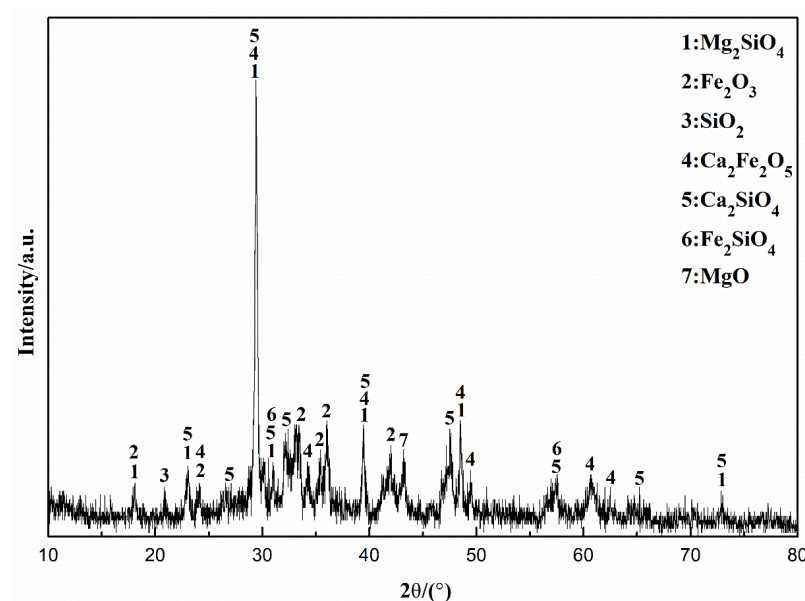


Figure 7. XRD patterns (MS).

2.3.2. Sample Characterization

The mineral phases in the samples were analyzed using XRD. XRD parameters were: scanning angle 10–80°, step scan mode with a step size of 0.02°, dwell time per step 0.24 s, tube voltage 40 kV, tube current 30 mA, and a Cu target X-ray tube. The microstructure and morphology of the samples were observed using SEM with energy dispersive spectroscopy (EDS) and backscattered electron (BSE) mode at an accelerating voltage of 15 kV. Finally, the size and quantity ratio of spinel were measured using a laser particle size analyzer.

2.3.3. Thermodynamic Calculations

FactSage 8.0 was used for thermodynamic analysis of the compositions in Table 2. The main thermodynamic calculation parameters in FactSage for this experiment were: temperature range 1000 °C~1500 °C, oxygen partial pressure $P(\text{O}_2) = 0.21$ atm, and total pressure 1 atm, using the FactPS and FToxid databases.

3. Results and Discussion

3.1. Effect of Fe_2O_3 on the Modification

Figure 8 presents the XRD patterns of the roasted F-series samples. The F-series samples represent compositions with increasing total Fe_2O_3 content, from 24.06 wt% in F1 to 33.96 wt% in F4. All four groups generated spinel and dicalcium silicate after roasting. Combining Figures 9 and 10, as the total Fe_2O_3 content increases, the main diffraction peak intensity of spinel first increases and then decreases, while the diffraction peaks of calcium ferrites gradually increase in intensity. In samples F3 and F4, with relatively high total Fe_2O_3 contents of 30.97 and 33.96 wt%, respectively, small amounts of magnesioferrite (MgFe_2O_4) were detected, and residual Fe_2O_3 was found in F4, consistent with thermodynamic calculations. From a phase-composition perspective, excessively high Fe_2O_3 content promotes calcium ferrite formation, thereby reducing the relative contents of silicates and spinel.

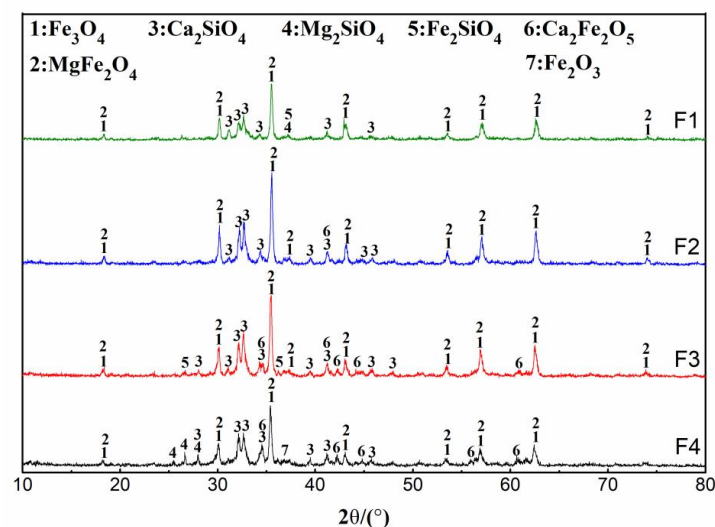
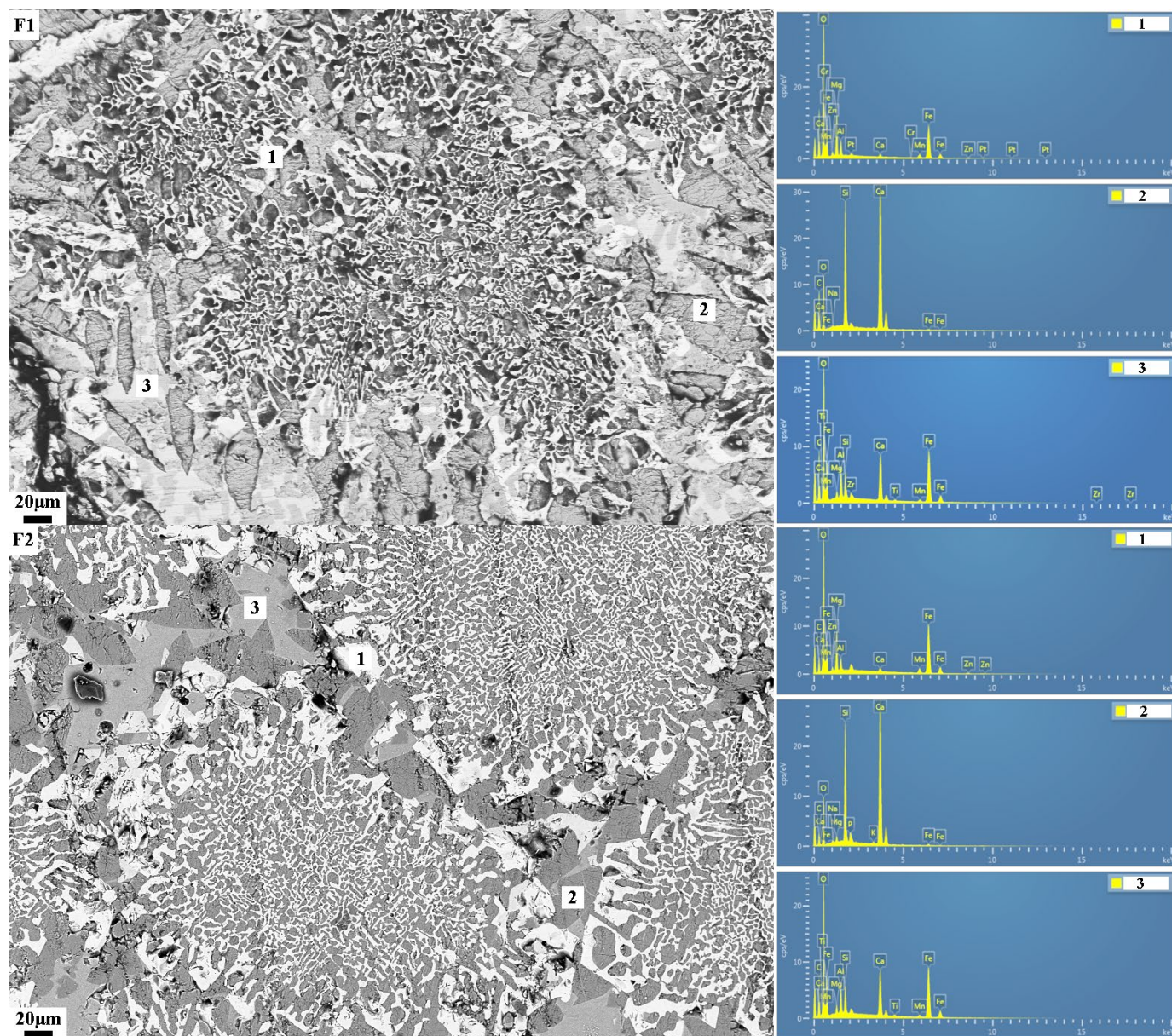


Figure 8. XRD patterns of F1–F4 with increasing total Fe_2O_3 contents.

Figure 9 shows the micro-morphology and EDS spectra of roasted mixed slags with different Fe_2O_3 contents. The local EDS atomic percentages of selected regions are listed in Table 3, and Figure 10 compares the local semi-quantitative EDS results. In all four samples (F1–F4), bright regions assigned to spinel (Region 1), dark gray silicate phases (Region 2), and light gray calcium ferrite-rich regions (Region 3) can be observed. The identification of Region 3 was based mainly on EDS point analysis combined with BSE contrast, rather than grayscale contrast alone; local grayscale differences may arise from compositional variation and sample-preparation effects. As total Fe_2O_3 content increases, calcium ferrite-rich regions become more evident, and eutectic/dendritic-like structures appear more clearly in F3 and F4. These structures are related to the increased diffusion flux and reduced eutectic interlamellar spacing under higher Fe_2O_3 contents. According to the local EDS results, the calcium ferrite-rich regions in F3 and F4 are close to CaFe_2O_4 , which is consistent with the thermodynamic calculations. Therefore, different modification strategies may be required for slags with different iron grades; within the tested range, moderate Fe_2O_3 addition favors spinel formation, whereas excessive Fe_2O_3 promotes calcium ferrite formation and spinel refinement. For example, when the iron content is around 25%, an appropriate amount of slag with higher iron content should be added to adjust the iron grade to about 30%. This yields a mineral composition with coarser-grained spinel, more silicate content, and less calcium ferrite phase, resulting in a concentrate with higher iron grade after magnetic separation. For slags with higher iron

content, slags with lower iron content can be blended to adjust, aiming to obtain coarser and more abundant spinel and silicate phases, avoiding excessive calcium ferrite formation.



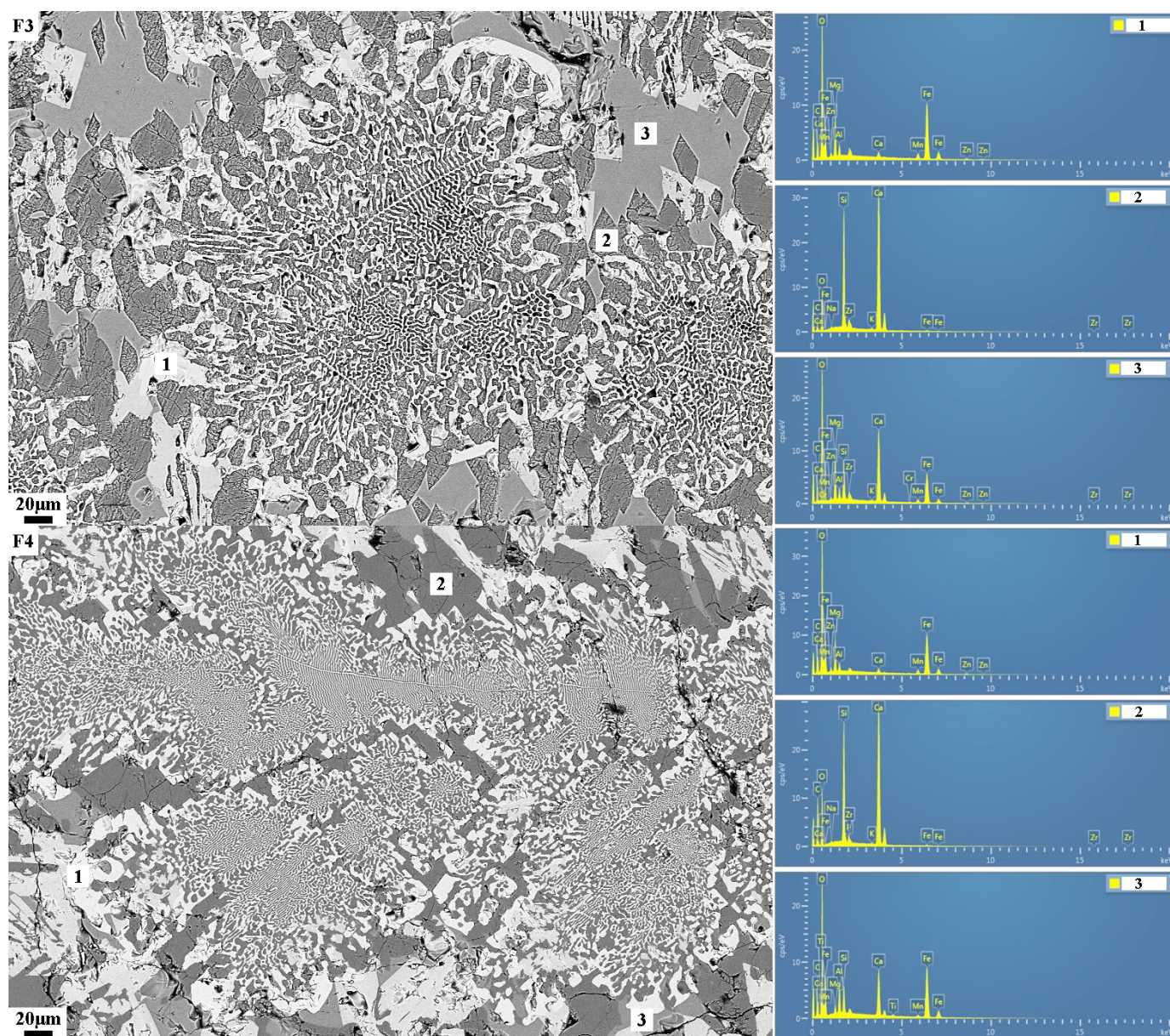


Figure 9. SEM images and EDS analysis of modified slags with different total Fe_2O_3 contents: (F1) sample with 24.06 wt% total Fe_2O_3 . (F2) sample with 27.66 wt% total Fe_2O_3 . (F3) sample with 30.97 wt% total Fe_2O_3 . (F4) sample with 33.96 wt% total Fe_2O_3 .

Table 3. Local EDS atomic percentages of selected regions in Figure 9.

Samples	No.	Element (%)				
		O	Si	Ca	Fe	Mg
F1	1	47.02	0	0.42	17.19	6.17
	2	39.13	7.62	15.20	0.20	0.14
	3	43.50	1.60	4.84	10.76	0.74
F2	1	46.8	0	0.37	16.97	6.02
	2	46.94	10.07	20.55	0.40	0.63
	3	45.12	0.72	5.52	10.96	0.57
F3	1	34.36	0	0.56	16.82	4.97
	2	43.16	10.00	20.90	0.22	0
	3	40.25	0.23	7.72	8.63	1.17
F4	1	42.91	0	0.37	11.22	3.48
	2	33.61	6.38	13.24	0.18	0
	3	42.88	1.22	5.02	11.01	0.52

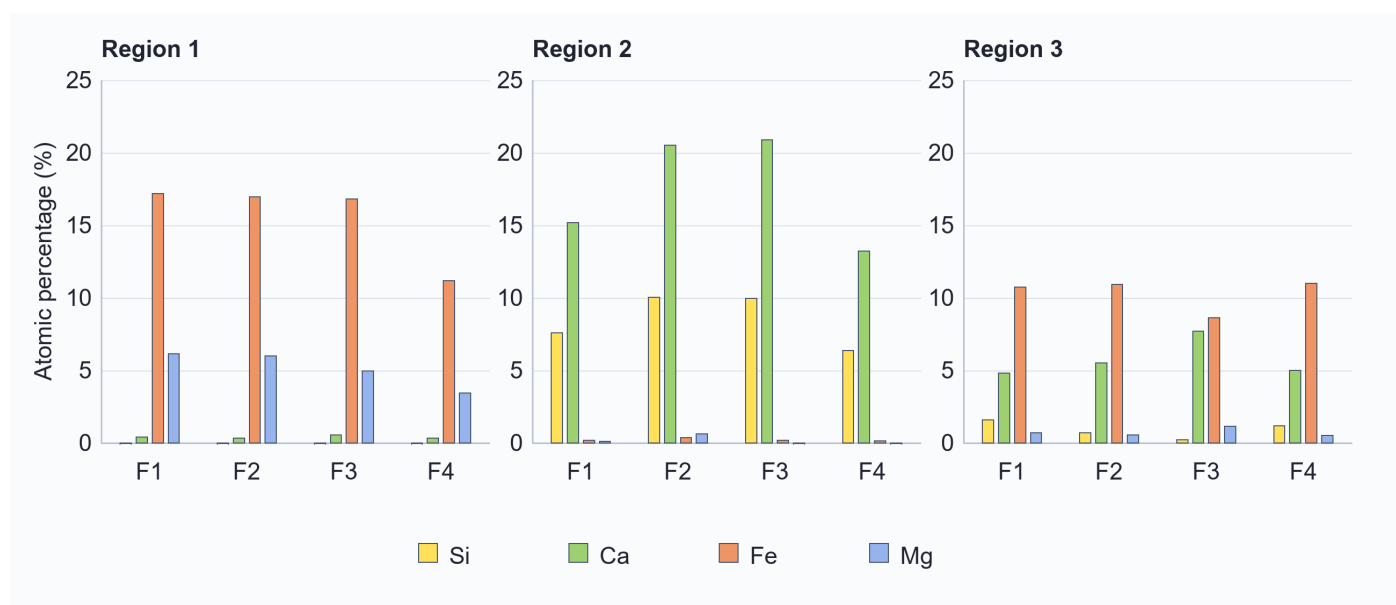


Figure 10. Local EDS comparison for the Fe_2O_3 series; O is omitted to highlight Si, Ca, Fe, and Mg.

Figure 11 shows the spinel particle size distribution in the F-series samples, in which the total Fe_2O_3 content increases from 24.06 to 33.96 wt%. As total Fe_2O_3 content increases, the spinel grain size first coarsens slightly and then refines. This size change is due to increased diffusion flux in the system caused by higher iron content, slightly increasing spinel growth. However, with further increase in Fe_2O_3 content, especially in F3 and F4 with total Fe_2O_3 contents of 30.97 and 33.96 wt%, eutectic structures appear abundantly. The increased iron content raises the system's diffusion rate, increasing the interface migration rate of eutectic lamellae, reducing interlamellar spacing, and resulting in finer spinel. The particle size distribution of F4 is slightly larger than that of F3 because F4 has Fe_2O_3 present in the low-temperature region. These pre-precipitated Fe_2O_3 particles act as nucleation sites for spinel solid-state phase transformation. MgO can directly combine with Fe_2O_3 via diffusion to form $\text{MgO-Fe}_2\text{O}_3$ type spinel. Under higher iron content conditions, the system's diffusion flux is larger, and MgO diffusion is faster, so the spinel size in F4 is relatively larger than in F3.

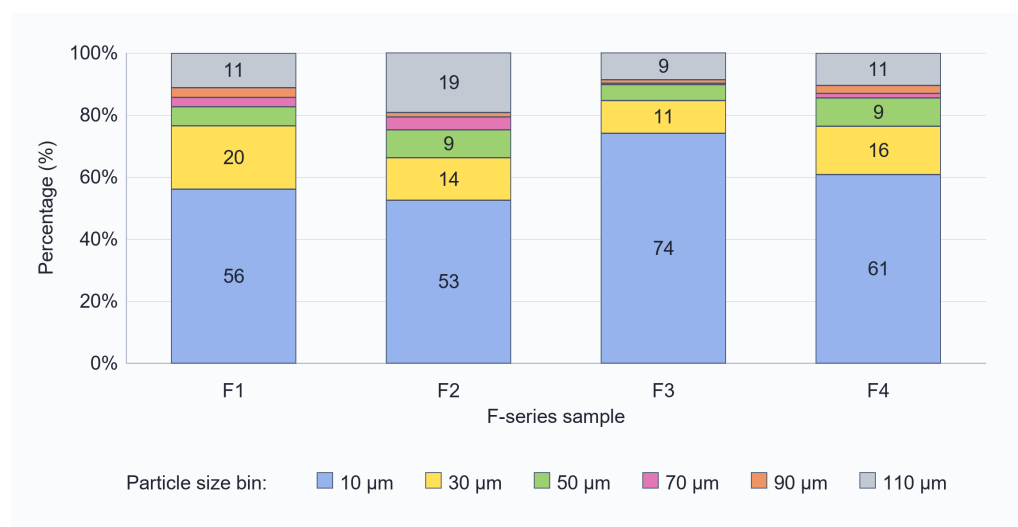


Figure 11. Particle size distribution of spinel in mixed slag with different total Fe_2O_3 contents.

3.2. Effect of MgO on the Modification

Figure 12 shows that all four mixed slag groups generated spinel and dicalcium silicate after sintering. As shown in Figure 12, as MgO content increases, the main diffraction peak intensities of spinel and dicalcium silicate first increase and then decrease. In M4 with the highest MgO content, an amorphous hump appears. In M2 and M3, due to higher MgO content, small amounts of magnesium silicates were detected by XRD, and a small amount of merwinite was detected in M3, consistent with thermodynamic calculations. Therefore, an appropriate MgO content promotes spinel and silicate formation, but excessively high MgO leads to a large portion of silicates existing in amorphous form after water quenching, making them unsuitable for direct use as building materials. Under the sintering conditions of this study, the total MgO content should be controlled within a relatively low range; among the tested M-series samples, 7.56 wt% MgO gave the best magnetic separation performance, whereas total MgO contents of 9.34 wt% and 11.05 wt% promoted merwinite/amorphous phases and spinel refinement.

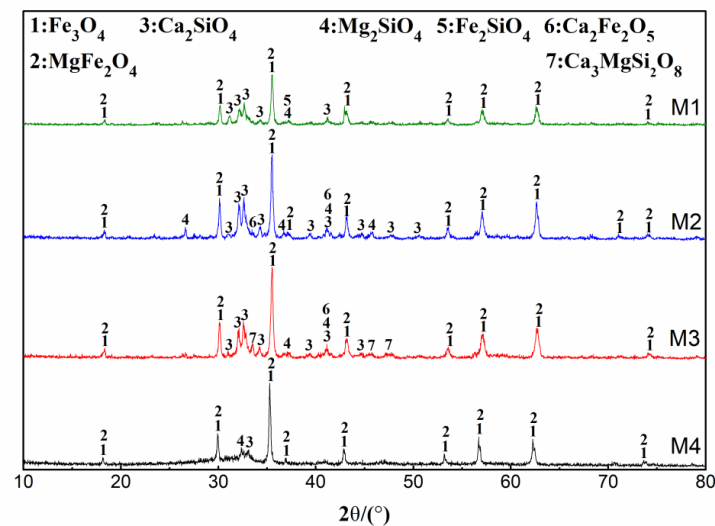
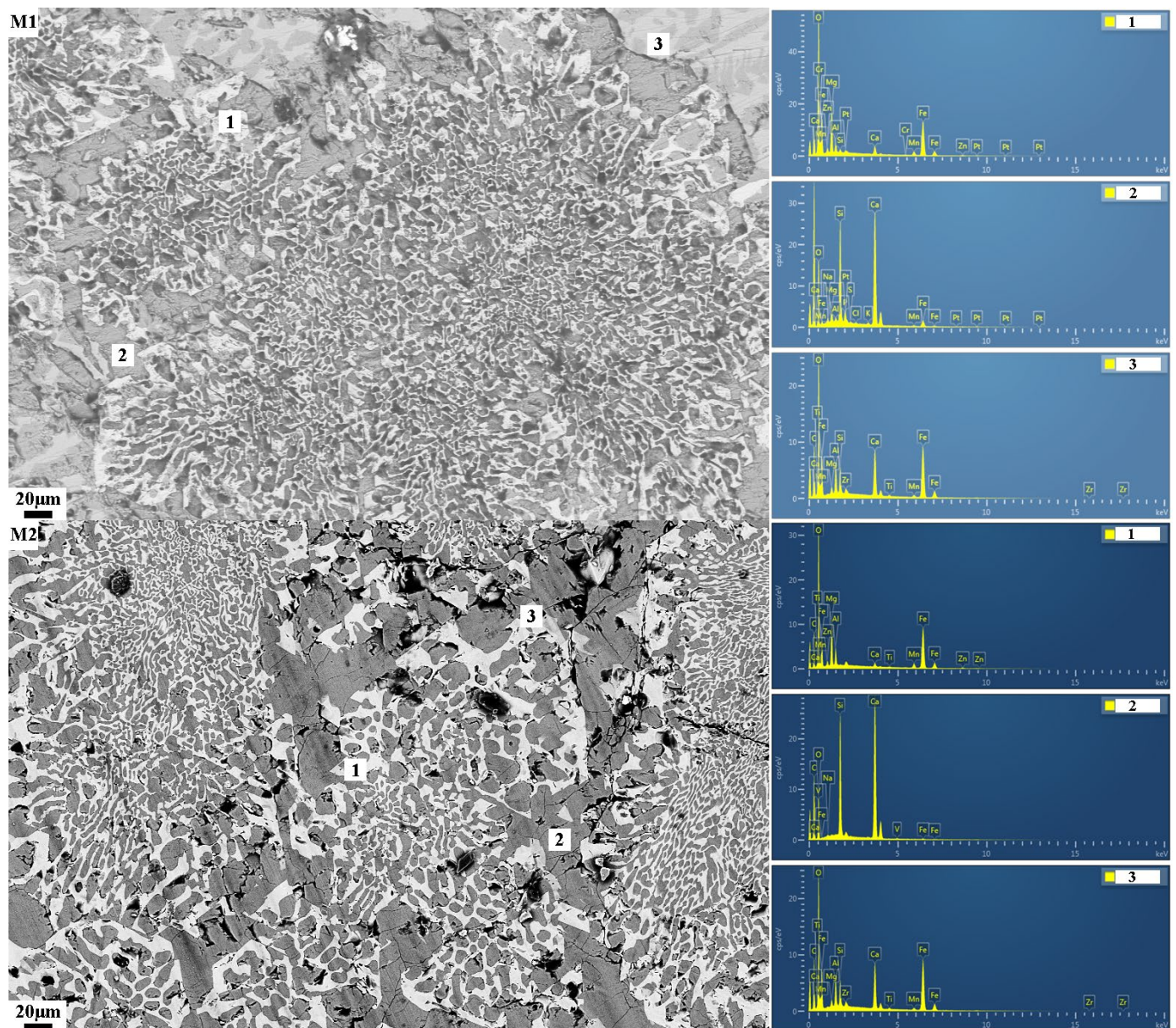


Figure 12. XRD patterns of M1–M4.

Figure 13 shows the micro-morphology and EDS spectra of roasted mixed slags with different MgO contents, and Figure 14 compares the local semi-quantitative EDS results. The SEM images provide qualitative microstructural observations, while the EDS point analyses in Table 4 provide local semi-quantitative compositional information for selected regions. Combining Figures 13 and 15, as total MgO content increases from 5.71 to 11.05 wt%, the spinel grain size first increases from M1 to M2 and then decreases in M3 and M4. This is because M4 has higher MgO content, allowing precipitation of iron-magnesium monoxides even in the low-temperature region. These monoxides become substrates for heterogeneous nucleation of spinel, causing extensive nucleation and increasing the nucleation rate; as shown in Figure 15, M4 contains 71.57% particles in the 10 μm bin and 86.69% particles within 30 μm , indicating spinel refinement. In M4 with higher MgO content, the silicate phase contains dissolved magnesium, appearing as a solid solution of dicalcium silicate and merwinite, consistent with thermodynamic calculations. The hump observed in the XRD pattern of M4 indicates a considerable amount of amorphous phase. From the perspective of eutectic structures, increased MgO content raises the system's diffusion flux, increasing the migration rate of eutectic lamellar interfaces, ultimately reducing interlamellar spacing and increasing the fraction of fine spinel particles within 30 μm . Considering all four samples, for the mixed slag system, lower MgO content avoids massive generation of merwinite and calcium ferrites, but spinel remains relatively fine.

With moderate MgO content, spinel can grow relatively coarse. Such coarse spinel is less likely to be entrapped by silicate phases, yielding a concentrate with higher iron grade after magnetic separation. With high MgO content, spinel becomes excessively fine. Fine spinel entrapped with silicate leads to lower iron grade in the concentrate after magnetic separation. High MgO content also shifts silicates towards merwinite formation, accompanied by some calcium ferrite generation. Excessively high MgO can amorphize the silicate component. These phenomena are unfavorable for the application of tailings in fields like building materials.



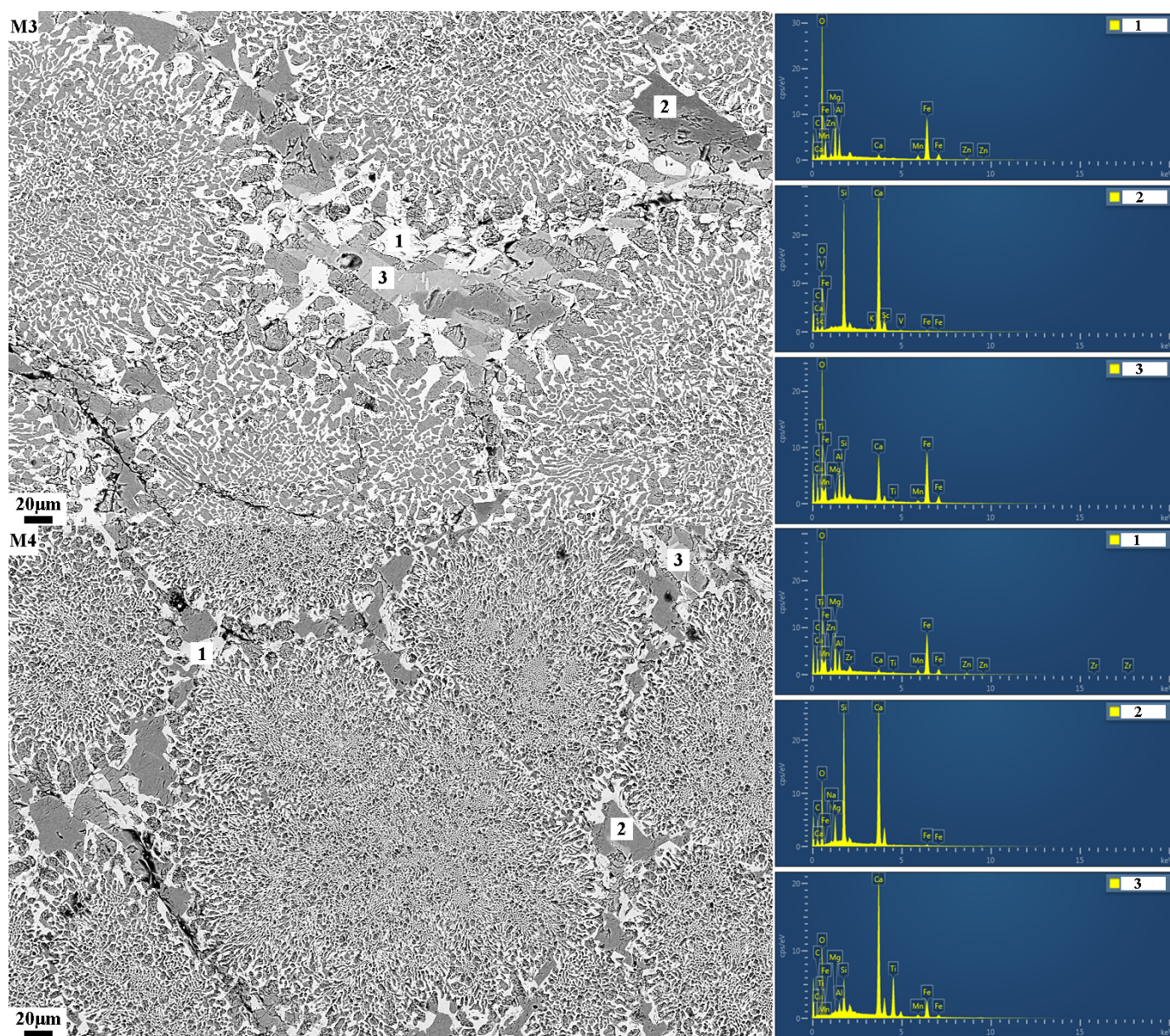


Figure 13. SEM images and EDS analysis of modified slags with different total MgO contents: (M1) sample with 5.71 wt% total MgO. (M2) sample with 7.56 wt% total MgO. (M3) sample with 9.34 wt% total MgO. (M4) sample with 11.05 wt% total MgO.

Table 4. Local EDS atomic percentages of selected regions in Figure 13.

Samples	No.	Element (%)				
		O	Si	Ca	Fe	Mg
M1	1	46.81	0	0.53	16.92	6.36
	2	40.25	8.02	16.83	0.32	0.20
	3	38.23	1.27	3.86	4.27	0.56
M2	1	42.49	0	0.37	10.80	4.60
	2	29.32	6.53	13.22	0.15	0
	3	38.92	0.95	4.02	4.96	0.23
M3	1	47.72	0	0.44	14.45	6.56
	2	46.58	8.48	16.46	0.10	0
	3	40.02	0.56	4.43	5.01	0.38
M4	1	42.79	0	0.33	10.85	4.80

2	43.50	8.77	15.32	0.26	2.08
3	43.18	1.96	12.97	4.13	0.21



Figure 14. Local EDS comparison for the MgO series; O is omitted to highlight Si, Ca, Fe, and Mg.

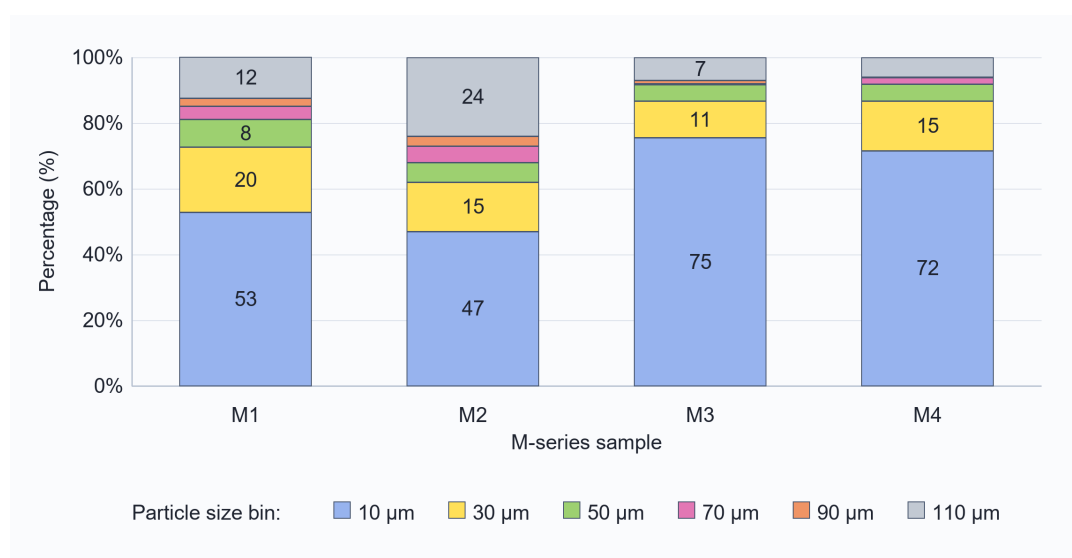


Figure 15. Particle size distribution of spinel in mixed slag with different total MgO contents.

3.3. Magnetic Separation

Figure 16 summarizes the magnetic separation yield, concentrate iron grade, and iron recovery rate of the F-series and M-series samples.

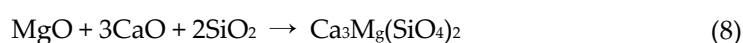
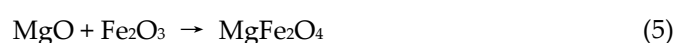
- (1) For the F-series samples, the Fe_2O_3 values discussed here refer to the total Fe_2O_3 contents in the mixed slag after blending and reagent addition. As the total Fe_2O_3 content increases from 24.06 to 33.96 wt%, the iron grade of the concentrate generally increases because of the increased iron input. For magnetic separation yield and iron recovery rate, both increase first and then decrease. This phenomenon is caused by changes in spinel particle size due to variations in iron content. When iron content increases from F1 to F2, the spinel grain size in the modified mixed slag becomes relatively coarser, making spinel less likely to be entrapped by silicate phases. Therefore, most spinel can be recovered, increasing the magnetic separation yield and iron

recovery rate for F2. With further increase in iron content, eutectic structures appear abundantly. Increased iron reduces the interlamellar spacing of eutectic structures, making spinel in F3 and F4 finer and more easily entrapped. Some fine spinel cannot be recovered by magnetic separation, causing both yield and recovery rate to decrease. For F4, which has the highest iron content, the concentrate after magnetic separation has the highest iron grade, exceeding 30%. However, due to very fine spinel, some spinel cannot be magnetically recovered, and some recovered spinel carries excessive silicate phases, resulting in high concentrate iron grade but low iron recovery rate for F4. Therefore, within the investigated F-series compositions, the sample with a total Fe_2O_3 content of 27.66 wt% showed the best combined magnetic separation performance. Compared with the baseline F1 sample, F2 increased the concentrate iron grade from 27.40% to 28.40% and the iron recovery rate from 91.06% to 92.27%, corresponding to increases of 1.00 and 1.21 percentage points, respectively. Compared with F4, which gave the minimum recovery rate of 86.29%, the recovery rate of F2 was higher by 5.98 percentage points.

- (2) As MgO content increases, the magnetic separation yield of the concentrate first decreases then increases, while the concentrate iron grade and iron recovery rate first increase and then decrease. M2 has relatively low MgO content, yet its concentrate has higher iron grade and recovery rate. M4 has the highest MgO content; although its magnetic separation yield is high, its concentrate has the lowest iron grade and recovery rate. This is due to differences in spinel particle size. For M2, with MgO content higher than M1 but lower than M3 and M4, the growth rate of spinel exceeds its nucleation rate, resulting in relatively coarse spinel. After mechanical crushing, it is less entrapped by silicates, leading to lower magnetic separation yield but higher concentrate iron grade. For M4, with the highest MgO content, the nucleation rate of spinel in the mixed slag greatly increases, far exceeding the growth rate, resulting in very fine spinel easily entrapped by silicates. These entrapped silicates are recovered along with spinel, causing high magnetic separation yield but low concentrate iron grade and recovery rate. Based on comprehensive magnetic separation results and phase analysis, the best tested MgO content is 7.56 wt%. Under this condition, the mixed slag exhibits favorable phase composition and magnetic separation results. Compared with the baseline M1 sample, M2 increased the concentrate iron grade from 27.76% to 29.11% and the iron recovery rate from 91.77% to 93.27%, corresponding to increases of 1.35 and 1.50 percentage points, respectively. Compared with M4, which produced the minimum recovery rate of 87.60% and the lowest concentrate iron grade of 23.35%, M2 improved the iron recovery rate and concentrate iron grade by 5.67 and 5.76 percentage points, respectively.

3.4. Reaction Mechanisms

Under the condition of maintaining a mass ratio of steel slag: copper slag: magnesium slag at 37:37:26 and adjusting the basicity (CaO/SiO_2) to 2.0, mixed roasting was conducted with the addition of Fe_2O_3 and MgO. The primary reaction mechanisms are as follows:



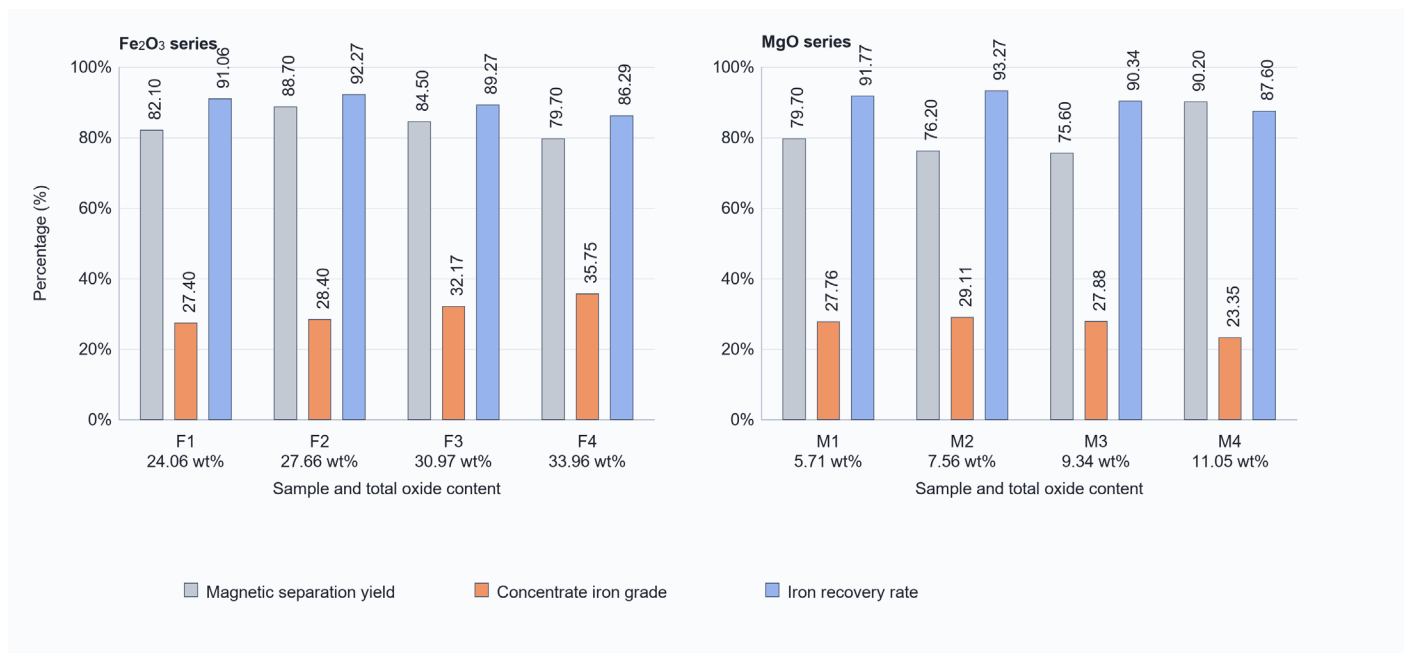


Figure 16. Magnetic separation yield, concentrate iron grade, and iron recovery rate of mixed slags with different total Fe₂O₃ and MgO contents.

Iron in copper and steel slags predominantly exists as fayalite (Fe₂SiO₄), which exhibits its weak magnetic properties and is challenging to recover via direct magnetic separation [18]. Although the generated magnetite (Fe₃O₄) is inherently ferromagnetic, the newly formed magnetite crystals under specific high-temperature oxidizing environments often present as fine grains intermingled with gangue phases. Furthermore, non-stoichiometric deviations can lead to insufficient contrast in magnetic susceptibility [19]. These factors typically result in the aggregation of magnetic particles and the entrainment of non-magnetic phases, adversely affecting recovery efficiency.

The solid-state reaction between MgO and iron oxides in the slag produces magnesium ferrite (MgFe₂O₄). This phase is characterized by strong ferrimagnetic and high magnetic susceptibility, making it the primary target mineral phase for iron recovery. Simultaneously, the combination of CaO and SiO₂ at high temperatures forms dicalcium silicate (Ca₂SiO₄), a non-magnetic phase. This allows for effective separation from the spinel phase during magnetic separation, achieving the enrichment of iron resources.

Appropriate additions of Fe₂O₃ and MgO facilitate the formation of the spinel phase. However, excessive addition promotes reactions (7) and (8), yielding calcium ferrite (CaFe₂O₄) and merwinite (Ca₃Mg(SiO₄)₂). Calcium ferrite has lower magnetic susceptibility than the target spinel phase and therefore tends to report to the non-magnetic tailings, causing iron loss and reducing the iron recovery rate, as shown by the decrease in recovery from 92.27% (F2) to 86.29% (F4) and from 93.27% (M2) to 87.60% (M4) at excessive Fe₂O₃ or MgO contents in Figure 16. The formation of the latter consumed CaO and SiO₂, thereby negatively impacting their potential value as supplementary cementitious materials.

4. Conclusions

Guided by the “waste-treats-waste” philosophy of a green circular economy, this study proposes a novel method for the synergistic modification of ternary smelting slags (steel slag, copper slag, and magnesium slag). Through thermodynamic calculations, phase transition analysis, and magnetic separation experiments, the modification mecha-

nism and resource utilization pathways were investigated in depth. The primary conclusions are as follows:

- (1) By leveraging the compositional complementarity of the three slags (utilizing copper slag to supplement iron and magnesium slag to supplement calcium and magnesium), the resource scarcity inherent in single-slag modification was effectively addressed. This approach achieves the one-time synergistic disposal of multiple large-scale industrial solid wastes without the need for significant amounts of costly external reagents.
- (2) The research demonstrates that by precisely modulating the Fe_2O_3 and MgO content, the transformation of weakly magnetic fayalite in the mixed slag into a strongly ferromagnetic magnesioferrite-based spinel solid solution $((\text{Mg}, \text{Fe})\text{Fe}_2\text{O}_4)$ can be achieved. This process effectively inhibits the formation of calcium ferrite by-products. Simultaneously, optimizing the spinel grain size prevents silicate inclusions caused by ultra-fine grains, thereby enhancing the grade of the magnetic concentrate.
- (3) Within the investigated F-series compositions, the sample with a total Fe_2O_3 content of 27.66 wt% showed the best combined magnetic separation performance, with a concentrate iron grade of 28.40% and an iron recovery rate of 92.27%. This value represents the best tested composition rather than a universal optimum.
- (4) Within the investigated M-series compositions, the sample with a total MgO content of 7.56 wt% showed the best magnetic separation performance, with a concentrate iron grade of 29.11% and an iron recovery rate of 93.27%. Additional experiments with narrower composition intervals are required to determine a more precise optimum range.
- (5) The modified magnetic concentrate has good economic and industrial application value in industries such as steelmaking and powder metallurgy, effectively alleviating the supply pressure on domestic iron ore resources. The resulting tailings, rich in silicates (e.g., Ca_2SiO_4), have the potential for manufacturing ceramics, glass-ceramics, cement, and concrete applications.

In summary, this study provides a theoretical foundation for the high-value utilization of various smelting slags and offers insights into phase transformation control and cross-industry synergistic resource recovery within complex solid-waste systems. The optimal composition range should be further refined through additional experiments with smaller Fe_2O_3 and MgO intervals.

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