The objective of this research was to optimize the comprehensive utilization of vanadium converter slag through targeted enrichment and stabilization of heavy metal vanadium. Employing the non-equilibrium solidification theory and FactSage software, we investigated the potential of modifying vanadium converter slag. When the original slag failed to generate vanadium-rich spinel with usable V contents, introducing modifying agents Fe and Al proved effective. Fe facilitated the enrichment of Cr within spinel, while Al significantly promoted the V enrichment. Expanding on this, we systematically examined the influence of Fe₂O₃, Al₂O₃, and MgO contents on spinel phase precipitation during vanadium slag solidification. The addition of Al resulted in the precipitation of corundum, hematite, spinel, olivine, and diopside phases. With an increase in the Fe₂O₃ content, the precipitation of Fe₃V₄O₁₁ and Mg₃V₂O₇ initially increased, reaching 9.67% before subsequently decreasing. Maintaining the Fe₂O₃ content within a range of 25–30% proved optimal for enhancing vanadium precipitation and enrichment. In contrast, variations in the Al₂O₃ content had minor impacts on SP-V phase precipitation, with slight effects on Fe₃V₄O₁₁ reaching 10.34%. Furthermore, the incorporation of MgO facilitated the precipitation of Mg₃V₂O₇ while concurrently suppressing the Fe₃V₄O₁₁ precipitation. By judiciously controlling the MgO content at approximately 20% enrichment, vanadium enrichment in the form of Fe₃V₄O₁₁ and Mg₃V₂O₇ spinel phases reached a remarkable 94.46%.

Keywords: vanadium, converter slag, enrichment, stabilization, non-equilibrium solidification

1 INTRODUCTION

Vanadium, as a rare metal element, finds wide application due to its high melting point, hardness, and toughness, in fields such as materials, steel production, aerospace, and petrochemicals, and is crucial for strategic resources worldwide.¹ ² Presently, over 90% of vanadium resources are sourced from vanadium-titanium magnetite, with vanadium slag (V₂O₅) being obtained through iron reduction processes.³ Depending on iron smelting methods, production stages, and slag treatment approaches, the chemical composition of vanadium slag varies. Common oxide components in most vanadium slags include Fe₂O₃, V₂O₅, SiO₂, MgO, MnO, and TiO₂, along with minor amounts of CaO, Cr₂O₃, and P₂O₅. The diverse chemical composition of vanadium slag influences its phase composition, which in turn affects subsequent processes for vanadium and chromium extraction.⁴ ⁶ Common phases in the low-calcium vanadium slags include Fe₂O₃, V₂O₅, SiO₂, MgO, MnO, and TiO₂, while vanadium is primarily present in forms like Fe₃V₄O₁₁, Mg₃V₂O₇, and V₂O₅. When chromium and vanadium exist as Al₂O₃ spinels, they exhibit enhanced oxi-

OPTIMIZING VANADIUM CONVERTER SLAG UTILIZATION: TARGETED ENRICHMENT AND STABILIZATION OF VANADIUM THROUGH NON-EQUILIBRIUM SOLIDIFICATION

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dation resistance, reduced susceptibility to acid-base corrosion, and effective suppression of chromium leaching.\textsuperscript{11–13} Al\(_2\)O\(_3\) in vanadium slag reacts with MgO and Cr\(_2\)O\(_3\) to form solid solutions like Mg(Cr\(_3\)Al\(_{1-x}\))\(_2\)O\(_4\), aiding in lowering the Cr\(_2\)O\(_3\) content and positively influencing chromium enrichment and stabilization.\textsuperscript{12,13} Moreover, spinel precipitation is closely related to temperature, with higher temperatures promoting spinel formation.\textsuperscript{14–16} Tang et al.\textsuperscript{17} found that at temperatures below 1540 °C, the slag contains an amorphous material and iron-aluminum spinel, while at 1580 °C, enriched chromium iron-aluminum spinel begins to precipitate, validating the above viewpoint. Wang\textsuperscript{20} studied the effects of B\(_2\)O\(_3\) on vanadium slag, observing that the spinel phase size increased with a higher B\(_2\)O\(_3\) content, with most chromium enriched in the spinel phase. Engstrom et al.\textsuperscript{21} indicated that higher masses of MgO and Fe\(_2\)O\(_3\) in slag favor increased chromium spinel phase precipitation, underscoring the significant influence of the MgO and Fe\(_2\)O\(_3\) content on chromium spinel precipitation in vanadium slag. Additionally, researchers like Cao and Pan\textsuperscript{18–20} investigated the impact of alkalinity on chromium enrichment in vanadium slag, finding that an alkalinity of 1.5 was beneficial for chromium enrichment in the spinel phase, with a nearly 100% enrichment observed at a temperature of 1300 °C.

Consequently, investigating the selective enrichment and stabilization of vanadium-chromium elements in spinel phases within vanadium slag holds critical significance for enhancing resource utilization and promoting green metallurgical manufacturing.\textsuperscript{22–26} This study, based on the vanadium slag composition and thermodynamic principles, employs the FactSage 8.2 thermodynamic software to simulate the solidification process of the Fe\(_2\)O\(_3\)-SiO\(_2\)-TiO\(_2\)-V\(_2\)O\(_5\)-Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\)-MgO slag system. The analysis explores the influence of the Fe\(_2\)O\(_3\) content on the spinel phase precipitation behavior, thereby providing a theoretical foundation for the enrichment of vanadium-chromium elements and efficient resource utilization in steel slag.

2 EXPERIMENTAL PART

2.1 FactSage simulation conditions

The Sheil-Gulliver solidification model is an approximate model for complex melt solidification processes, assuming infinite-fast element diffusion in the liquid phase and zero diffusion rate in the solid phase. During the cooling process, the solid-liquid interface always maintains the local equilibrium state. The liquid and solid phase compositions at the interface can be calculated based on the system phase equilibrium, and the composition of the solid phase remains constant after its formation, while the liquid phase maintains a uniform composition. Based on the non-equilibrium solidification theory of the melt, i.e., the Sheil-Gulliver equation, using the thermodynamic software FactSage 8.2 and relevant databases, the Fe\(_2\)O\(_3\)-SiO\(_2\)-TiO\(_2\)-V\(_2\)O\(_5\)-Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\)-MgO slag system’s phase equilibrium during solidification was simulated. The influence of the Fe\(_2\)O\(_3\) content on the precipitation behavior of the spinel phase during slag cooling was investigated. The simulation calculation employed the following database, compound and precipitation phase settings: (1) Databases: FToxide, FactPS; (2) Compound settings: ideal gas, pure solid; (3) Liquid phase settings: FToxide-SLAGA, FToxide-SPINA, FToxide-Mel_A, FToxide-aC2SA, FToxide-bC2SA, FToxide-Mel_A, FToxide-OlivA, FToxide-Cord, FToxide-Mull, FToxide-CORU, FToxide-SP-V, FToxide-TiO\(_2\), with the cooling calculation set to Shell-Gulliver cooling in FToxide-SLAGA. The simulation calculation was performed in a temperature range of 1000–2000 °C with a step size of 10 °C, and the system calculation pressure was set to 1.013 × 10\(^5\) Pa. To validate the thermodynamic calculation results, a comparison was conducted between experimental outcomes of the SP-V generation in vanadium slag. This was performed to corroborate the effects of Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\) and MgO on the vanadium enrichment behavior within the slag.

3 RESULTS AND DISCUSSION

3.1 Simulation of S0 slag

In accordance with the compositional range of vanadium slag from steel plants, a base vanadium slag material with a mass of 100 g was designed. The composition is as follows: w(Fe\(_2\)O\(_3\)) = 55 %, w(SiO\(_2\)) = 15 %, w(TiO\(_2\)) = 10 %, w(V\(_2\)O\(_5\)) = 10 %, w(Al\(_2\)O\(_3\)) = 4 %, w(Cr\(_2\)O\(_3\)) = 3 %, and w(MgO) = 3 %, as shown in Figure 1. The non-equilibrium solidification process of the S0 base slag was simulated using the Shell-Gulliver solidification model.

| Table 1: Composition of S0 slag mixture (g) |
|-----------------|-------|-------|-------|-------|-------|
| ID  | Fe\(_2\)O\(_3\) | SiO\(_2\) | TiO\(_2\) | V\(_2\)O\(_5\) | Al\(_2\)O\(_3\) | Cr\(_2\)O\(_3\) | MgO |
| S0  | 55     | 15     | 10     | 10     | 4      | 3      | 3    |

From Figure 1, it can be observed that SPINA is a spinel phase containing chromium (Cr) elements, while SP-V is a spinel phase containing vanadium (V) elements. In the SPINA phase, the main constituents are Fe\(_2\)Cr\(_2\)O\(_6\), MgCr\(_2\)O\(_4\), MgAl\(_2\)O\(_4\), and MgFe\(_2\)O\(_4\). However, there is no precipitation of the SP-V phase. In the SP-V phase, the main constituents are Fe\(_2\)V\(_2\)O\(_7\), Mg\(_3\)V\(_2\)O\(_8\), FeAl\(_2\)O\(_4\), MgAl\(_2\)O\(_4\), and MgFe\(_2\)O\(_4\). The precipitation of chromium-rich spinel is very low, at 3.39 %. Within the SPINA phase, precipitation fractions of MgCr\(_2\)O\(_4\) and FeCr\(_2\)O\(_4\) containing Cr are 0.0013 % and 0.000708 %, respectively, which is almost negligible. Similarly, within the SP-V phase, the precipitation fractions of Mg\(_3\)V\(_2\)O\(_8\) and Fe\(_2\)V\(_2\)O\(_7\) are both 0, which can be attributed to the lack of FeO generation in the S0 slag system. This phenomenon is supported by the studies by X.-P. ZHANG et al.: OPTIMIZING VANADIUM CONVERTER SLAG UTILIZATION: TARGETED ENRICHMENT...
Su et al.\textsuperscript{13} and Yu et al.\textsuperscript{27} To address the issue of vanadium not precipitating in the form of a spinel phase and to increase the precipitation of spinel with larger and more concentrated growth, we introduced Fe and Al elements into the slag system as the reducing agents. Thermodynamic simulations were conducted for this combination of slag systems.

3.2 Simulation with Fe and Al additions in S0 slag

Based on the composition range of steel mill vanadium slag, the basic vanadium slag with a mass of 100 g was designed. Fe and Al elements were separately added to the slag to investigate the influence of different compositions on the precipitation behavior of the SP-V phase. The goal was to identify effective reducing agents to enhance the yield of vanadium precipitation in the slag. The simulated slag compositions are presented in Table 2.

The thermodynamic calculations reveal that the addition of Fe and Al to the S0 original slag can achieve a high proportion of the SP-V phase, including types like FeV$_2$O$_4$ and MgV$_2$O$_4$. However, we need to further investigate the influence of different Fe and Al contents on the enrichment of vanadium in the spinel phase. Figure 2 presents the impact of a varying Fe content on the precipitation of the SP-V phase in the S0 slag system. It is observed that with the Fe content below 10%, the precipitation fraction of the SP-V phase gradually increases,

![Figure 1: Mineral phase composition and SPINA phase precipitation fraction during solidification of S0 base slag system](image)

![Table 2: Slag compositions with Fe and Al additions (g)](table)

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Figure 2: Precipitation fractions of the SP-V phase after the addition of Fe and Al to the S0 slag.

Figure 3: Precipitation fractions of spinel phases after adding Fe and Al to S0 slag.
and the critical precipitation temperature also rises, indicating a positive correlation. However, when the Fe content exceeds 10%, the precipitation fraction of the SP-V phase decreases, and the critical precipitation temperature reduces, revealing a negative correlation. Hence, controlling the Fe content within a range of 10–15% during the vanadium extraction process could effectively enhance the vanadium yield. Furthermore, the addition of Al to the S0 slag also promotes the precipitation of vanadium in the spinel phase. The data in Figure 2 demonstrate that when Al is below 13.5%, the precipitation fraction of the SP-V phase continues to increase with the increasing Al content, along with a rise in the critical precipitation temperature, indicating a positive correlation. However, when the Al content surpasses 13.5%, the precipitation fraction of the SP-V phase decreases, and the critical precipitation temperature also decreases, showing a negative correlation. Therefore, restricting the Al content within a range of 13.5–15% during the vanadium extraction process could enhance the vanadium yield. The precipitation process of the SP-V phase is generally completed at around 1050 °C.

From Figure 3, it can be observed that the FeV2O4 precipitation fraction gradually increases as the Fe content rises from 5% to 25%, with a notable increment when Fe reaches 25%, resulting in a precipitation fraction of approximately 5.5%. This is concurrent with a significant enrichment of vanadium within the FeV2O4 phase. Similarly, with the addition of Al to the S0 slag, the precipitation fraction of FeV2O4 initially increases and then decreases as Al increases. The maximum precipitation fraction of FeV2O4 is achieved at an Al content of 13.5%, reaching around 9.86%. This also leads to a pronounced enrichment of vanadium in the FeV2O4 spinel phase. For MgV2O4, when the Fe content exceeds 10%, some vanadium starts to be present in the FeV2O4 phase, causing a decrease in its precipitation fraction. This consequently results in a slight reduction in the overall SP-V phase precipitation, accounting for approximately 50% of the total precipitation. The enrichment of vanadium within the FeV2O4 phase also experiences a slight decrease. When Al is added to the S0 slag, with the Al content below 15%, the precipitation fraction of MgV2O4 gradually increases with an increasing Al content, peaking at 1.87% when Al reaches 15%. However, with further increases in the Al content, the precipitation fraction of MgV2O4 diminishes. This behavior is attributed to the partial presence of vanadium in the FeV2O4 spinel phase, causing a decrease in the precipitation fraction of the MgV2O4 spinel phase.

3.3 Summary

(1) When adding Al to S0 slag with an Al content of 12.5 g, the mass of MgV2O4 and FeV2O4 containing V elements increased from 0 g to 1.338 g and 9.9587 g, respectively. The precipitation rate of V in spinel reached 94.46%, indicating a significant role of Al in promoting the V enrichment in spinel during industrial vanadium recovery processes. (2) When adding Fe to S0 slag with a Fe content of 25 g, the mass of MgCr2O4 and FeCr2O4 containing Cr elements increased from 0.000708 g and 0.00103 g to 3.25 g and 0.47 g, respectively. The precipitation rate of Cr in spinel reached 86%. This highlights the importance of the Fe content in enhancing the enrich-
ment of Cr in spinel, particularly in the growth of MgCr$_2$O$_4$ and FeCr$_2$O$_4$, during industrial chromium recovery processes. (3) Based on (1) and (2), it is evident that the reducing agent Fe is more favorable for increasing the precipitation fraction of chromite and promoting the growth of MgCr$_2$O$_4$ and FeCr$_2$O$_4$, leading to the enrichment of Cr in spinel. On the other hand, the reducing agent Al significantly enhances the growth of the SP-V phase, resulting in superior precipitation of MgV$_2$O$_4$ and FeV$_2$O$_4$ and promoting the enrichment of V in spinel.

3.4 Vanadium spinel precipitation behavior in vanadium slag

To explore the detailed impact of adding Fe and Al to S0 slag on the precipitation behavior of vanadium spinel, and based on the conclusions drawn earlier, the effect of adding Al is examined. The Sheil-Gulliver solidification model is used to simulate the non-equilibrium solidification of S0 basic slag with an addition of 12.5 g Al. The slag composition includes \( w(\text{Fe}_2\text{O}_3) = 55 \% \), \( w(\text{SiO}_2) = 15 \% \), \( w(\text{TiO}_2) = 10 \% \), \( w(\text{V}_2\text{O}_5) = 10 \% \), \( w(\text{Al}_2\text{O}_3) = 4 \% \), \( w(\text{Cr}_2\text{O}_3) = 3 \% \), and 12.5 g Al. The results are presented in Figure 4. During the slag solidification process, the main precipitated phases include corundum, hematite, spinel, olivine, and diopside. Both chromite and SP-V phases, which contain chromium, are high-temperature precipitates. In the solidification of the S0 basic slag, the starting temperature for the precipitation of these two phases slightly differs by 1460 °C for chromite and 1340 °C for SP-V. As the temperature decreases, the chromite phase reaches its maximum precipitation fraction of 20.4 % when the temperature drops to 1160 °C. On the other hand, the SP-V phase achieves its maximum precipitation fraction of approximately 42.5 % at 1090 °C. The Al$_4$FeSi$_5$O$_{18}$ and Al$_4$MgSi$_5$O$_{18}$ phases start to precipitate at around 1230 °C, with precipitation fractions increasing from 0 % to 0.10 and 0.56 %, respectively. When the temperature drops to 1190 °C, the precipitation fraction of Al$_4$MgSi$_5$O$_{18}$ no longer increases, reaching a maximum value of 9.8 %. Finally, at 1150 °C, the precipitation fraction of Al$_4$MgSi$_5$O$_{18}$ stops increasing, with the maximum value being 1.88 %.

The SPINA phase consists of solid solutions, primarily composed of FeAl$_2$O$_4$, MgFe$_2$O$_4$, MgCr$_2$O$_4$, FeCr$_2$O$_4$, and minor amounts of CrAl$_2$O$_4$ and CrFe$_2$O$_4$. After the completion of solidification, the total precipitation fraction of the SPINA phase is 16.59 %, with the FeAl$_2$O$_4$ content of 6.35 %, MgFe$_2$O$_4$ content of 2.04 %, FeCr$_2$O$_4$ content of 3.96 %, and MgCr$_2$O$_4$ content of 1.09 %. In contrast, the SP-V phase has a slightly different composition, primarily replacing MgCr$_2$O$_4$ and FeCr$_2$O$_4$ with FeV$_2$O$_4$ and MgV$_2$O$_4$. The composition of the SP-V phase includes FeAl$_2$O$_4$ at 13.56 %, MgFe$_2$O$_4$ at 2.38 %, FeV$_2$O$_4$ at 10.12 %, and MgV$_2$O$_4$ at 2.67 %. Additionally, the SPINA phase contains trace amounts of spinel-type CrO·Cr$_2$O$_3$ chromite (0.05 %), FeO$_3$ inverse spinel (0.21 %), and minor amounts of MgFe$_2$O$_4$, CrFe$_2$O$_4$, and CrAl$_2$O$_4$ spinel phases. In this study, a controlled variable method was employed (keeping other variables constant except for the Fe$_2$O$_3$ content variation). Thus, the primary focus is on investigating the impact of the Fe$_2$O$_3$ content on the precipitation of SPINA and SP-V phases in the slag system. Therefore, the following sections will primarily analyze the changes in
precipitation fractions and onset temperatures of spinel phases, including MgCr₂O₄, FeCr₂O₄, FeV₂O₄, and MgV₂O₄.

Figure 5 shows the changes in the Cr and V contents in the slag and spinel phases during the solidification of the basic slag system S0, and the standard Gibbs free energy of formation for four types of spinel phases. As the temperature drops to 1550 and 1350 °C, respectively, the contents of Cr and V in the spinel phase begin to increase; upon complete solidification of the S0 base slag at 1000 °C, the mass fraction of Cr in the spinel phase is 1.46 %. Calculations show that the mass fraction of Cr in the spinel phase is 2.05 %, suggesting that in theoretical conditions, chromium is entirely present in the chromite phase. Additionally, the mass fraction of V in the spinel phase is 5.2 %. Calculations reveal that the mass fraction of V in the base slag with 3-% Cr₂O₃ is 2.05 %, indicating that the precipitation rate of Cr in the chromite phase is 71.4 %. The mass fraction of chromium in the oxide (CrO₃) is also 2.05 %, suggesting that in theoretical conditions, chromium is entirely present in the chromite phase. Additionally, the mass fraction of V in the spinel phase is 5.2 %. Calculations reveal that the mass fraction of V in the spinel phase is 2.05 %, indicating that the precipitation rate of V in the spinel phase is 71.4 %.

From Figure 5, it is evident that at a certain temperature, MgCr₂O₄ is the most stable phase. Furthermore, previous studies demonstrated that the contents of Fe₂O₃, Al₂O₃, and MgO can influence the solubility of the FeCr₂O₄ spinel phase in slag. To enhance the enrichment of Cr and V elements in stable spinel phases within vanadium slag, providing favorable conditions for vanadium and chromium extraction from the original slag, adjustments in the slag’s elemental composition are necessary. These adjustments aim to promote the precipitation of chromium as MgCr₂O₄ and FeCr₂O₄ spinel phases while facilitating the precipitation of vanadium as the FeV₂O₄ spinel phase.

3.4 Vanadium slag composition design

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<tr>
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According to the composition range of steel mill vanadium slag, when adding 12.5 g of Al, a basic vanadium slag mass of 100 g is designed. On this basis, the Fe₂O₃, Al₂O₃, and MgO contents of the steel slag are varied to study the effect of different components on the phase separation behavior of SP-V. This provides a theoretical basis for a comprehensive utilization of vanadium slag. The simulated slag formulations are shown in Table 3.

3.5 Effects of three oxide contents on SP-V phase precipitation

Figure 6 shows the influences of Fe₂O₃, Al₂O₃, and MgO contents on the behavior of SP-V phase precipitation and the proportions of various spinel phases after solidification in vanadium slag. As depicted in Figure 6a, with an increase in the Fe₂O₃ content from 32 % to 50 %, the starting precipitation temperature of the SP-V phase gradually increases, with a precipitation temperature range of 1200–1400 °C. During slag solidification, the amount of SP-V phase precipitation increases with the increasing Fe₂O₃ content, showing a positive correlation. The maximum precipitation amount is achieved with a Fe₂O₃ content of 50 %, reaching 30.82 %. This indicates a significant influence of the Fe₂O₃ content on the precipitation of the SP-V phase. From Figure 6a, showing the proportion of each component in the spinel phase, it is evident that FeV₂O₄ and FeAl₂O₄ constitute the highest proportion in the SP-V phase. With an increase in the Fe₂O₃ content, the proportion of MgV₂O₄ spinel in the SP-V phase initially increases and then decreases. When the Fe₂O₃ content is between 37 and 40 %, the proportion of MgV₂O₄ spinel in the SP-V phase reaches its maximum value of 15 %. Meanwhile, the proportion of FeV₂O₄ spinel in the SP-V phase decreases with the increase in the Fe₂O₃ content, declining from 48 to 34 %. The increased proportion of MgV₂O₄ spinel is attributed to the decreased proportion of FeV₂O₄ spinel. The proportion of FeAl₂O₄ also follows the pattern of initial decreasing and then increasing. As previously analyzed, under certain temperatures, FeV₂O₄ is more stable than FeAl₂O₄. FeV₂O₄ and MgV₂O₄ spinels are preferable solid chromium phases. Therefore, maintaining Fe₂O₃ at 37–40 % (minimizing the proportion of FeAl₂O₄) is conducive to the precipitation of vanadium in the form of FeV₂O₄ spinel. As indicated in Figure 6b, an increase in the Al₂O₃ content slightly raises the starting precipitation temperature of the SP-V phase to a range of 1350–1410 °C. During solidification, the precipitation of the SP-V phase increases with an increase in the Al₂O₃ content, showing a positive correlation. However, the precipitation amount of the SP-V phase remains between 29.02 % and 31.43 %, suggesting a minor influence of the Al₂O₃.
content on the precipitation of the SP-V phase. Figure 6b includes a diagram showing the proportions of components in the spinel phase. With an increase in the $\text{Al}_2\text{O}_3$ content, the proportions of $\text{FeV}_2\text{O}_4$ and $\text{MgV}_2\text{O}_4$ spinels in the SP-V phase after solidification remain relatively unchanged. This implies that the changes in the $\text{Al}_2\text{O}_3$ content have a minimal impact on the proportions of various spinels in the SP-V phase. According to Figure 6c, when the $\text{MgO}$ content increases from 8 % to 25 %, the precipitation proportion of the SP-V phase initially increases, then decreases, and increases again. This indicates that a moderate $\text{MgO}$ content promotes the formation of the SP-V phase. Thus, maintaining the $\text{MgO}$ content at 10 % can facilitate the generation of the SP-V phase. According to Figure 6c, the proportion of each component in the spinel phase is plotted; with an increase in the $\text{MgO}$ content, the proportion of $\text{MgV}_2\text{O}_4$ spinel in the spinel phase increases from 12 % to 25 %, while the proportion of $\text{FeV}_2\text{O}_4$ spinel decreases from 39 % to 26 %. This implies that an increased $\text{MgO}$ content favors the enrichment of vanadium in the form of $\text{MgV}_2\text{O}_4$ spinel. Additionally, the content and proportion of $\text{MgAl}_2\text{O}_4$ spinel will also experience a substantial increase. In conclusion, a higher $\text{MgO}$ content promotes the precipitation of $\text{MgV}_2\text{O}_4$ while inhibiting the precipitation of $\text{FeV}_2\text{O}_4$, making $\text{MgO}$ an effective regulator of the composition of the SP-V phase.

3.6 $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, and $\text{MgO}$ content effects on $\text{FeV}_2\text{O}_4$ and $\text{MgV}_2\text{O}_4$ spinel phase precipitation in slag

The influences of $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, and $\text{MgO}$ contents on the precipitation behavior of $\text{FeV}_2\text{O}_4$ and $\text{MgV}_2\text{O}_4$ spinel phases in the slag are depicted in Figure 7. As shown in Figure 7a, the precipitation fraction of the $\text{FeV}_2\text{O}_4$ spinel phase in the slag increases with a higher $\text{Fe}_2\text{O}_3$ content. When the $\text{Fe}_2\text{O}_3$ content reaches 50 %, the precipitation fraction of the $\text{FeV}_2\text{O}_4$ spinel phase reaches its maximum value of 9.668 %. This is due to a substantial reduction of $\text{Fe}_2\text{O}_3$ to $\text{FeO}$ in the slag, leading to the reaction of $\text{FeO}$ with $\text{V}_2\text{O}_3$ to form the $\text{FeV}_2\text{O}_4$ spinel phase. An increased $\text{FeO}$ content enhances the enrichment of the SP-V phase, further increasing the precipitation of the $\text{FeV}_2\text{O}_4$ spinel phase. According to the figure, the precipitation fraction of the $\text{MgV}_2\text{O}_4$ spinel phase initially increases and then decreases with the rising $\text{Fe}_2\text{O}_3$ content. The $\text{MgV}_2\text{O}_4$ spinel phase content increases from 0.08 % to 3.06 % as the $\text{Fe}_2\text{O}_3$ content rises to 40 %, and then decreases to 1.72 % with further increases in the $\text{Fe}_2\text{O}_3$ content. This suggests that the addition of $\text{Fe}_2\text{O}_3$ generally promotes the precipitation of the SP-V phase, especially the main component $\text{FeV}_2\text{O}_4$, and controlling the $\text{FeO}$ mass fraction within a range of 40–50 % is favorable for the precipitation of the $\text{FeV}_2\text{O}_4$ spinel phase and enrichment of vanadium in the spinel phase. Consequently, it can be inferred that the $\text{FeO}$ content is also a crucial factor influencing vanadium extraction in the slag system.

As illustrated in Figure 7b, the precipitation fraction of the $\text{FeV}_2\text{O}_4$ spinel phase increases with a higher $\text{Al}_2\text{O}_3$ content, showing a positive correlation. When the $\text{Al}_2\text{O}_3$ content reaches 20 %, the precipitation fraction of the $\text{FeV}_2\text{O}_4$ spinel phase reaches its maximum value of 10.347 %. This is attributed to $\text{Al}_2\text{O}_3$ promoting the generation of $\text{FeO}$, leading to an increase in the $\text{FeO}$ content.
in the slag, and subsequently enhancing the precipitation of the FeV₂O₄ spinel phase. The content of the MgV₂O₄ spinel phase increases and then decreases with the rising Al₂O₃ content. When the Al₂O₃ content increases to 8 %, the MgV₂O₄ spinel phase content increases from the original 1.15 to 1.23 %. Overall, the addition of Al₂O₃ plays a role in promoting the enrichment of vanadium in the SP-V phase, but its effect is not substantial. As the MgO content increases, the precipitation temperature for FeV₂O₄ increases while its precipitation fraction decreases, showing an inverse relationship. When the addition of MgO increases from 8 to 25 %, the precipitation temperature of FeV₂O₄ rises from 1350 °C to 1520 °C, and its precipitation fraction decreases from 8.16 % to 5.72 %, which is a significant reduction. At the same time, the precipitation temperature of MgV₂O₄ increases with the increase in MgO, and its precipitation amount also increases with the increase in the MgO content. Especially in the high-temperature region (>1200 °C), the rate of increase in the precipitation of MgV₂O₄ is considerable. At 1150 °C, when the MgO addition increases from 8 % to 25 %, the precipitation fraction of MgV₂O₄ increases from 2.55 % to 4.79 %, which is a moderate increase. Therefore, the promotion of MgV₂O₄ spinel precipitation by MgO comes at the expense of a reduction in the FeV₂O₄ precipitation, but overall, the enrichment of vanadium in the SP-V phase is still beneficial, so maintaining MgO at around 20 % is favorable for the enrichment of vanadium in the form of FeV₂O₄ and MgV₂O₄ spinel phases.

4 CONCLUSIONS

In the process of vanadium slag treatment, the presence of the S₀ original slag alone does not facilitate a substantial precipitation of high-content SPINA and SP-V phases, thus failing to achieve the enrichment of vanadium and chromium elements within spinel structures. Nevertheless, by introducing Al into the S₀ slag, with an Al content of 12.5 g, the mass of V-containing MgV₂O₄ and FeV₂O₄ increases from 0 g to 1.338 g and 9.9587 g, respectively. This results in the precipitation rate of V in spinel rising from 0 % to a remarkable 94.46 %. Simultaneously, an addition of Fe to the S₀ slag, with a Fe content of 25 g, causes the mass of Cr-containing MgCr₂O₄ and FeCr₂O₄ to rise from their original values of 0.000708 g and 0.00103 g to 3.25 g and 0.47 g, respectively, leading to a Cr precipitation rate within spinel structures of 86 %. Furthermore, during the solidification of vanadium slag with added Fe and Al, prominent phases that form include Al₄FeSi₅O₁₈, Al₄MgSi₅O₁₈, and spinel phases. The SP-V phase predominantly comprises MgV₂O₄ and FeV₂O₄, while the SPINA phase is primarily composed of MgCr₂O₄ and FeCr₂O₄. In general, the FeO content significantly affects the precipitation behavior of the SP-V phase. A moderate increase in FeO promotes the precipitation of FeV₂O₄ and MgV₂O₄. However, excessive FeO suppresses the precipitation of MgV₂O₄. The AlO₃ content influences the overall precipitation of the SP-V phase, with a moderate AlO₃ content facilitating the precipitation of FeV₂O₄ spinel, especially at an AlO₃ content of 20 %, where the precipitation rate of FeV₂O₄ reaches a maximum of 10.347 %. Nonetheless, the impact on the proportions of different spinel phases within the SP-V phase is minimal. With an increase in the MgO content, the proportion of MgV₂O₄ rises, while that of FeV₂O₄ decreases. Controlling the MgO content at around 20 % is advantageous for the enrichment of vanadium in the form of both FeV₂O₄ and MgV₂O₄ spinel phases. In conclusion, these interrelated factors collectively contribute
to an effective enrichment of vanadium and chromium elements within spinel structures in vanadium slag.

Acknowledgments

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