UDK 546.881:625.821.4
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 58(3)339(2024)

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

OPTIMIRANJE UPORABE VANADIJEVE KONVERTERSKE ŽLINDRE: CILJANA OBOGATITEV IN STABILIZACIJA S POMOČJO NERAVNOTEŽNEGA STRJEVANJA

Xiao-Pei Zhang, Jian-Bao Zhang, Li-Jie Peng, Ya-Jun Wang*, Jun-Guo Li

School of Metallurgy and Energy, North China University of Science and Technology, 063210 Tangshan, P. R. China

Prejem rokopisa – received: 2023-10-01; sprejem za objavo – accepted for publication: 2024-04-10

doi:10.17222/mit.2023.984

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 elements, 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 Fe_2O_3, Al_2O_3 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 Fe_2O_3 content, the precipitation of FeV_2O_4 and MgV_2O_4 initially increased, peaking at 9.67 % before subsequently decreasing. Maintaining the Fe_2O_3 content within a range of 25–30 % proved optimal for enhancing vanadium precipitation and enrichment. In contrast, variations in the Al_2O_3 content had minor impacts on SP-V phase precipitation, with slight effects on FeV_2O_4 reaching 10.34 %. Furthermore, the incorporation of MgO facilitated the precipitation of MgV_2O_4 while concurrently suppressing the FeV_2O_4 precipitation. By judiciously controlling the MgO content at approximately 20 %, vanadium enrichment in the form of FeV_2O_4 and MgV_2O_4 spinel phases reached a remarkable 94.46 %.

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

V članku avtorji opisujejo raziskavo optimizacije sestave vanadijeve konverterske žlindre za splošno uporabo s pomočjo ciljane obogatitve in stabilizacijo vanadija kot težke in okolju škodljive kovine. Z uporabo teorije neravnotežnega strjevanja in programskega orodja FactSage so raziskali potencialne možnosti za modifikacijo vanadijeve konverterske žlindre. Ker se v originalni žlindri ne tvori na vanadiju bogati špinel, ki porabi ves razpoložljivi vanadij, se z uvedbo modificiranja z dodatki kot sta železo (Fe) in aluminij (Al) le tega učinkovito porabi. Železo (Fe) pospeši obogatitev špinela s kromom (Cr), medtem ko aluminij močno pospeši njegovo obogatitev z vanadijem. Na osnovi tega so avtorji sistematično raziskali vplive vsebnosti Fe_2O_3, Al_2O_3 in MgO na izločanje špinelne faze med strjevanjem vanadijeve žlindre. Dodatek Al je povzročil izločanje (tvorbo) korunda, hematita, špinela, olivina in diopsidne faze. Povečanje vsebnosti Fe_2O_3 je v začetku povečalo nastajanje FeV_2O_4 in MgV_2O_4 do maksimalne vrednosti 9,67 %, nato pa je koncentracija obeh začela strmo upadati. Da bi pospešili izločanje in obogatitev špinela z vanadijem je potrebno ohranili koncentracijo Fe_2O_3 v mejah med 25% in 30%. Nasprotno pa ima variranje vsebnosti Al_2O_3 zanemarljiv vpliv na izločanje SP-V faze z rahlim učinkom na obogatitev z FeV_2O_4 do 10,34 %. Nadalje dodatek MgO pospeši nastanek in izločanje MgV_2O_4, kar pa takoj zavre izločanje FeV_2O_4. Z natančno kontrolo vsebnosti MgO pri približno 20 % so avtorji te raziskave dosegli pomembno 94,46 % vezavo vanadija in tako obogatitev žlindre s špinelnima fazama v obliki FeV_2O_4 in MgV_2O_4.

Ključne besede: vanadij, konverterska žlindra, obogatitev, stabilizacija, neravnotežno strjevanje

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 (V_2O_5) 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 Fe_2O_3, V_2O_5, SiO_2, MgO, MnO, and TiO_2, along with minor amounts of CaO, Cr_2O_3, and P_2O_5. 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 slag from converters include spinel, olivine and pyroxene, characterized as follows.

Chromium in vanadium slag mainly exists in forms such as Cr_2O_3, $MgCr_2O_4$, $FeCr_2O_4$, $CrAl_2O_4$ and $CrFe_2O_4$, while vanadium is primarily present in forms like FeV_2O_4, MgV_2O_4, and V_2O_3. When chromium and vanadium exist as AB_2O_4 spinels, they exhibit enhanced oxi-

*Corresponding author's e-mail:
wangyj@ncst.edu.cn (Ya-Jun Wang)

dation resistance, reduced susceptibility to acid-base corrosion, and effective suppression of chromium leaching.[7–11] Al_2O_3 in vanadium slag reacts with MgO and Cr_2O_3 to form solid solutions like $Mg(CrxAl_{1-x})O_4$, aiding in lowering the Cr_2O_3 content and positively influencing chromium enrichment and stabilization.[12,13] Moreover, spinel precipitation is closely related to temperature, with higher temperatures promoting spinel formation.[14–16] Tang et al.[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[20] studied the effects of B_2O_3 on vanadium slag, observing that the spinel phase size increased with a higher B_2O_3 content, with most chromium enriched in the spinel phase. Engstrom et al.[21] indicated that higher masses of MgO and Fe_2O_3 in slag favor increased chromium spinel phase precipitation, underscoring the significant influence of the MgO and Fe_2O_3 content on chromium spinel precipitation in vanadium slag. Additionally, researchers like Cao and Pan[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.[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_2O_3-SiO_2-TiO_2-V_2O_5-Al_2O_3-Cr_2O_3-MgO slag system. The analysis explores the influence of the Fe_2O_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_2O_3-SiO_2-TiO_2-V_2O_5-Al_2O_3-Cr_2O_3-MgO slag system's phase equilibrium during solidification was simulated. The influence of the Fe_2O_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[13]: (1) Databases: FToxide, FactPS; (2) Compound settings: ideal gas, pure solid; (3) Liquid phase settings: FToxide-SLAGA, FToxide-SPINA, FToxide-MeO_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 Sheil-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_2O_3, Al_2O_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: $w(Fe_2O_3)$ = 55 %, $w(SiO_2)$ = 15 %, $w(TiO_2)$ = 10 %, $w(V_2O_5)$ = 10 %, $w(Al_2O_3)$ = 4 %, $w(Cr_2O_3)$ = 3 %, and w (MgO) = 3 %, as shown in **Figure 1**. The non-equilibrium solidification process of the S0 base slag was simulated using the Sheil-Gulliver solidification model.

Table 1: Composition of S0 slag mixture (g)

ID	Fe_2O_3	SiO_2	TiO_2	V_2O_5	Al_2O_3	Cr_2O_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 $FeCr_2O_4$, $MgCr_2O_4$, $FeAl_2O_4$, $MgAl_2O_4$, and $MgFe_2O_4$. However, there is no precipitation of the SP-V phase. In the SP-V phase, the main constituents are FeV_2O_4, MgV_2O_4, $FeAl_2O_4$, $MgAl_2O_4$, and $MgFe_2O_4$. The precipitation of chromium-rich spinel is very low, at 3.39 %. Within the SPINA phase, precipitation fractions of $MgCr_2O_4$ and $FeCr_2O_4$ containing Cr are 0.0013 % and 0.000708 %, respectively, which is almost negligible. Similarly, within the SP-V phase, the precipitation fractions of MgV_2O_4 and FeV_2O_4 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

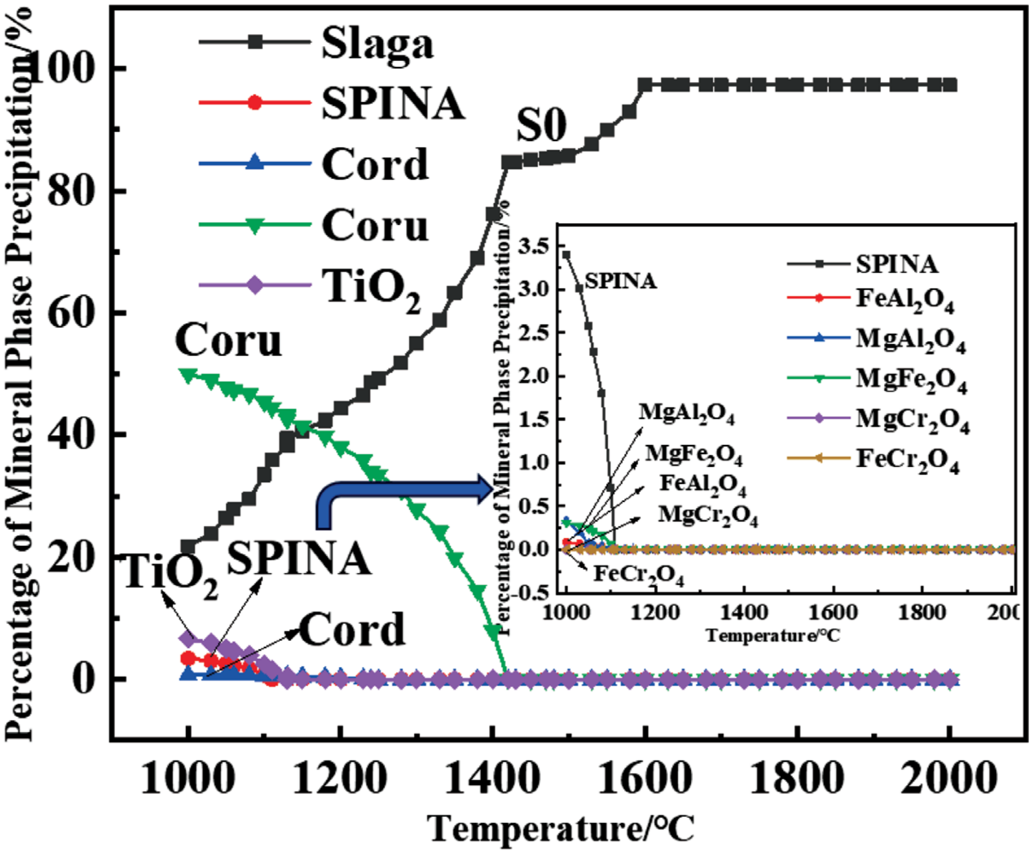

Figure 1: Mineral phase composition and SPINA phase precipitation fraction during solidification of S0 base slag system

Table 2: Slag compositions with Fe and Al additions (g)

ID	Fe_2O_3	SiO_2	TiO_2	V_2O_5	Al_2O_3	Cr_2O_3	MgO	Fe	Al
Fe1	55	15	10	10	4	3	3	5	–
Fe2	55	15	10	10	4	3	3	10	
Fe3	55	15	10	10	4	3	3	15	
Fe4	55	15	10	10	4	3	3	20	
Fe5	55	15	10	10	4	3	3	25	
AL1	55	15	10	10	4	3	3	–	10
AL 2	55	15	10	10	4	3	3		12.5
AL 3	55	15	10	10	4	3	3		13.5
AL 4	55	15	10	10	4	3	3		15
AL 5	55	15	10	10	4	3	3		20

Su et al.[13] and Yu et al.[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_2O_4 and MgV_2O_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,

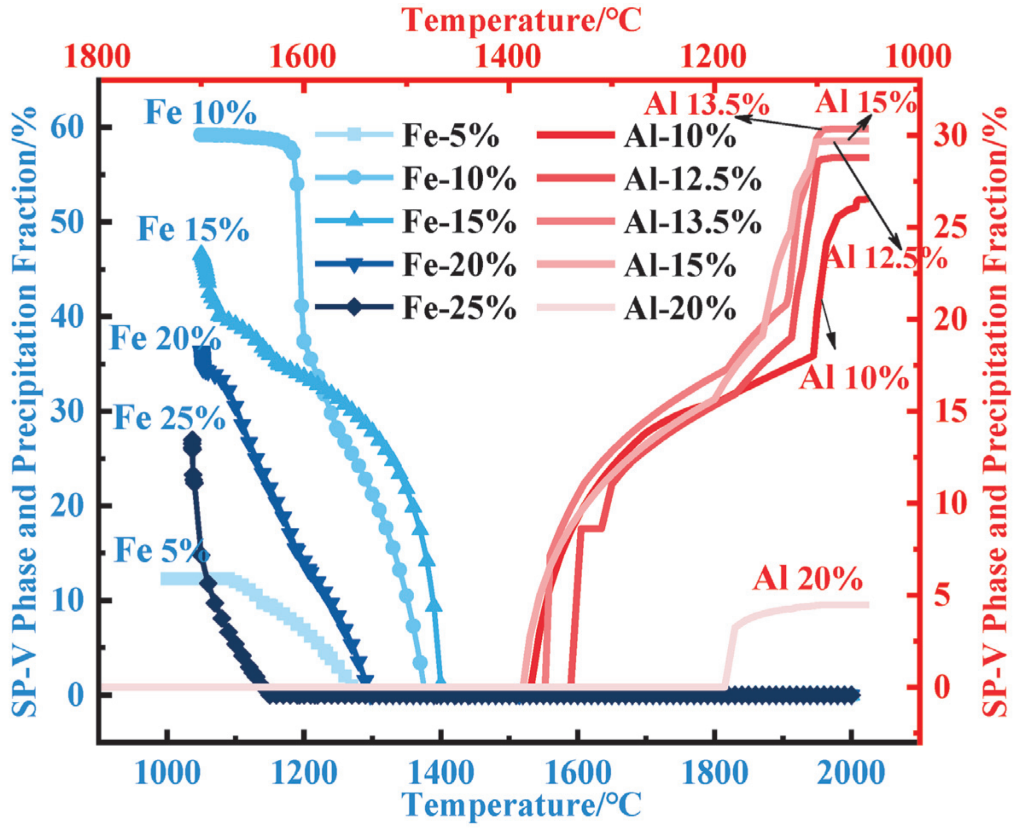

Figure 2: Precipitation fractions of the SP-V phase after the addition of Fe and Al to the S0 slag

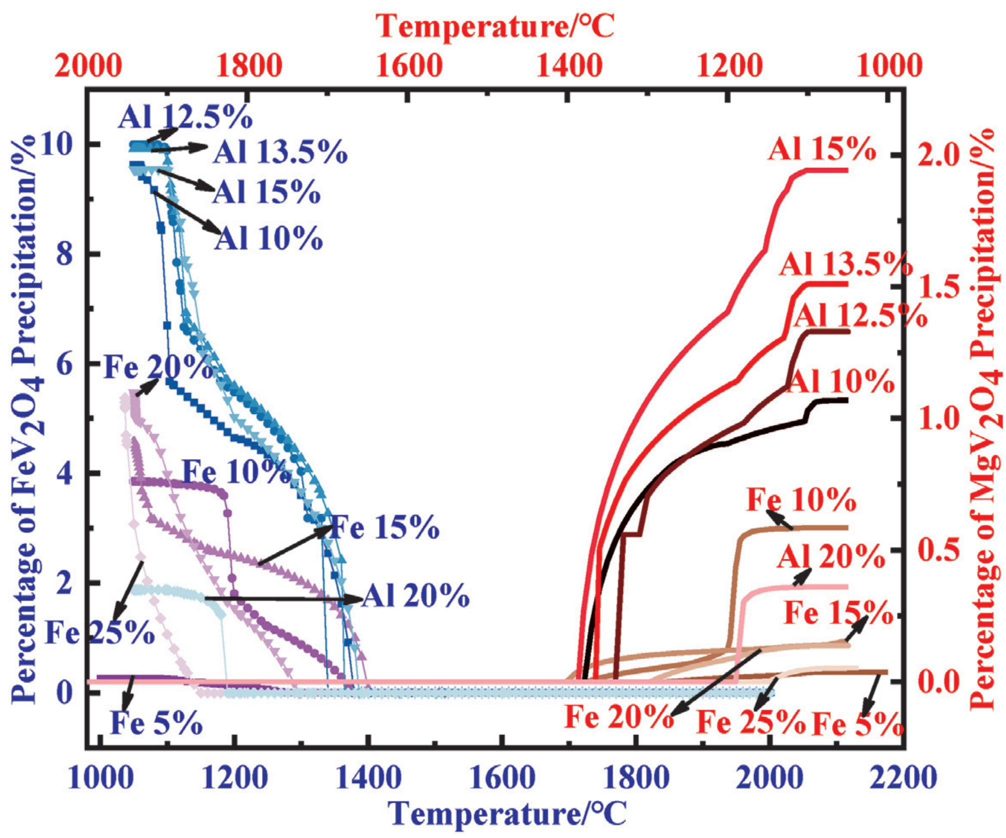

Figure 3: Precipitation fractions of spinel phases after adding Fe and Al to S0 slag

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 FeV_2O_4 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 FeV_2O_4 phase. Similarly, with the addition of Al to the S0 slag, the precipitation fraction of FeV_2O_4 initially increases and then decreases as Al increases. The maximum precipitation fraction of FeV_2O_4 is achieved at an Al content of 13.5 %, reaching around 9.86 %. This also leads to a pronounced enrichment of vanadium in the FeV_2O_4 spinel phase. For MgV_2O_4, when the Fe content exceeds 10 %, some vanadium starts to be present in the FeV_2O_4 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 FeV_2O_4 phase also experiences a slight decrease. When Al is added to the S0 slag, with the Al content below 15 %, the precipitation fraction of MgV_2O_4 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 MgV_2O_4 diminishes. This behavior is attributed to the partial presence of vanadium in the FeV_2O_4 spinel phase, causing a decrease in the precipitation fraction of the MgV_2O_4 spinel phase.

3.3 Summary

(1) When adding Al to S0 slag with an Al content of 12.5 g, the mass of MgV_2O_4 and FeV_2O_4 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 $MgCr_2O_4$ and $FeCr_2O_4$ 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-

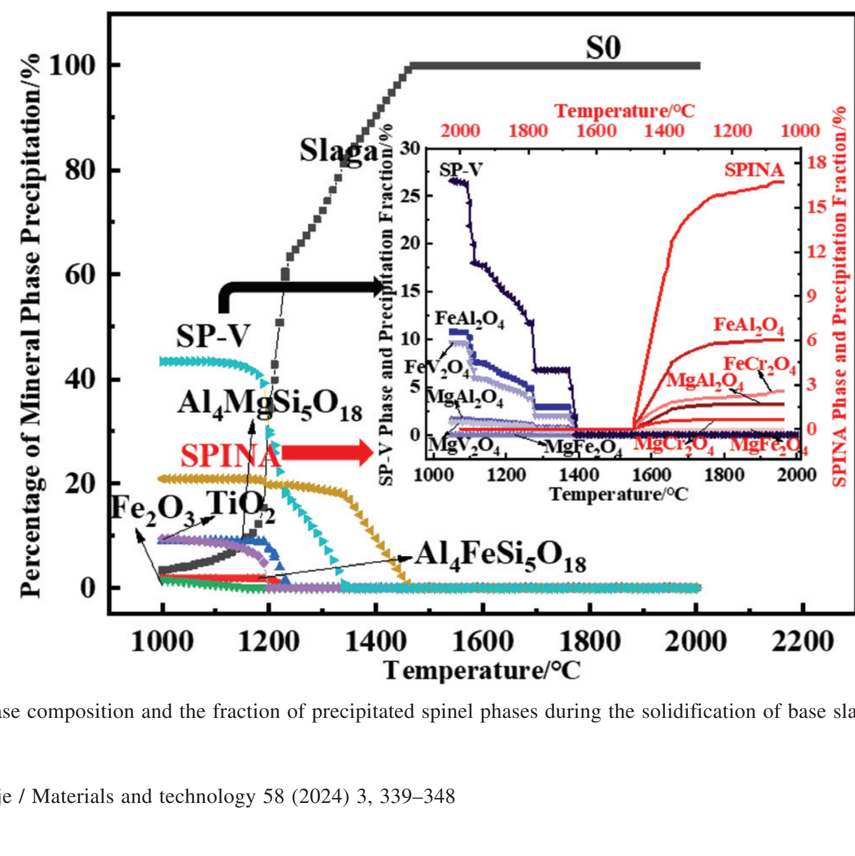

Figure 4: Mineral phase composition and the fraction of precipitated spinel phases during the solidification of base slag system S0 after the Al addition

ment of Cr in spinel, particularly in the growth of $MgCr_2O_4$ and $FeCr_2O_4$, 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 $MgCr_2O_4$ and $FeCr_2O_4$, 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_2O_4 and FeV_2O_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 $w(Fe_2O_3)$ = 55 %, $w(SiO_2)$ = 15 %, $w(TiO_2)$ = 10 %, $w(V_2O_5)$ = 10 %, $w(Al_2O_3)$ = 4 %, $w(Cr_2O_3)$ = 3 %, $w(MgO)$ = 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 $Al_4FeSi_5O_{18}$ and $Al_4MgSi_5O_{18}$ 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 $Al_4MgSi_5O_{18}$ no longer increases, reaching a maximum value of 9.8 %. Finally, at 1150 °C, the precipitation fraction of $Al_4MgSi_5O_{18}$ stops increasing, with the maximum value being 1.88 %.

The SPINA phase consists of solid solutions, primarily composed of $FeAl_2O_4$, $MgFe_2O_4$, $MgCr_2O_4$, $FeCr_2O_4$, and minor amounts of $CrAl_2O_4$ and $CrFe_2O_4$. After the completion of solidification, the total precipitation fraction of the SPINA phase is 16.59 %, with the $FeAl_2O_4$ content of 6.35 %, $MgFe_2O_4$ content of 2.04 %, $FeCr_2O_4$ content of 3.96 %, and $MgCr_2O_4$ content of 1.09 %. In contrast, the SP-V phase has a slightly different composition, primarily replacing $MgCr_2O_4$ and $FeCr_2O_4$ with FeV_2O_4 and MgV_2O_4. The composition of the SP-V phase includes $FeAl_2O_4$ at 13.56 %, $MgFe_2O_4$ at 2.38 %, FeV_2O_4 at 10.12 %, and MgV_2O_4 at 2.67 %. Additionally, the SPINA phase contains trace amounts of spinel-type $CrO{\cdot}Cr_2O_3$ chromite (0.05 %), Fe_3O_4 inverse spinel (0.21 %), and minor amounts of $MgFe_2O_4$, $CrFe_2O_4$, and $CrAl_2O_4$ spinel phases. In this study, a controlled variable method was employed (keeping other variables constant except for the Fe_2O_3 content variation). Thus, the primary focus is on investigating the impact of the Fe_2O_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

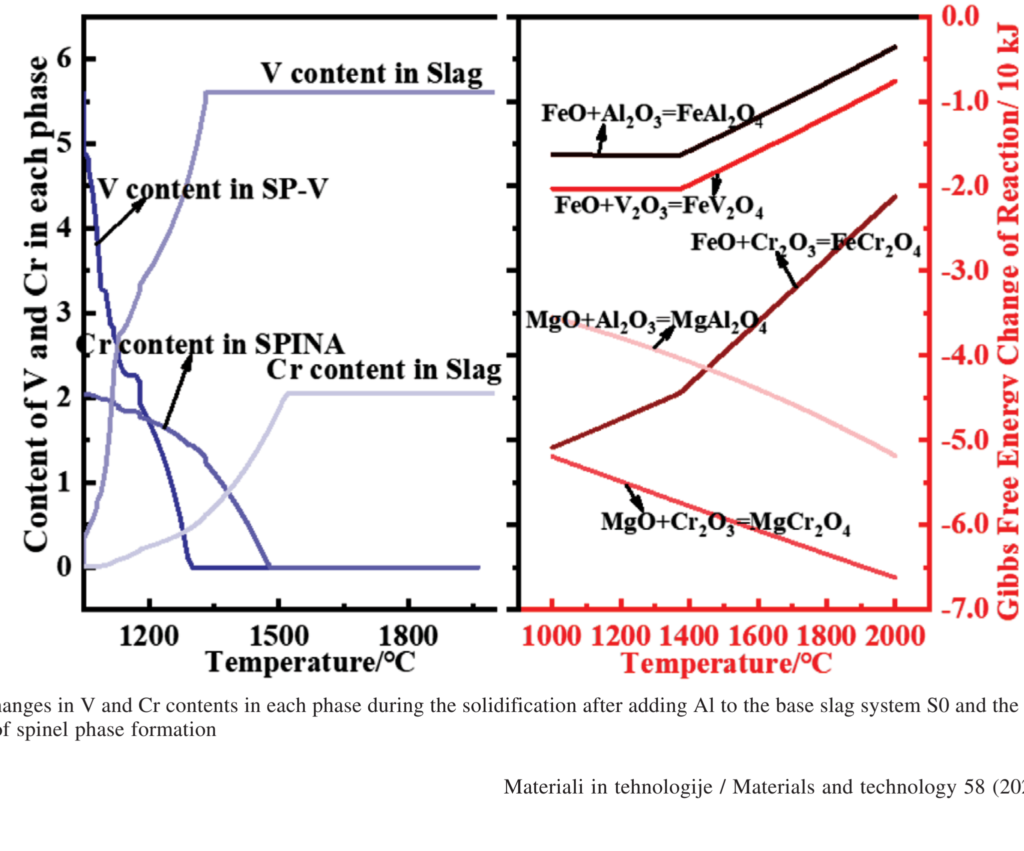

Figure 5: Changes in V and Cr contents in each phase during the solidification after adding Al to the base slag system S0 and the standard Gibbs free energy of spinel phase formation

precipitation fractions and onset temperatures of spinel phases, including $MgCr_2O_4$, $FeCr_2O_4$, FeV_2O_4, and MgV_2O_4.

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 base slag with 3-% Cr_2O_3 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 (CrO_x) is also 2.05 %, suggesting that in theoretical conditions, chromium is entirely present in the chromite phase.[28] 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 10-% V_2O_5 is 5.6 %, indicating that the precipitation rate of V in the SP-V phase is 94.46 %. Hence, it can be concluded that, in theoretical circumstances, vanadium is exclusively present in the SP-V phase.

From **Figure 5**, it is evident that at a certain temperature, $MgCr_2O_4$ is the most stable phase. Furthermore, previous studies demonstrated that the contents of Fe_2O_3, Al_2O_3, and MgO can influence the solubility of the $FeCr_2O_4$ spinel phase in slag.[13] 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 $MgCr_2O_4$ and $FeCr_2O_4$ spinel phases while facilitating the precipitation of vanadium as the FeV_2O_4 spinel phase.

3.4 Vanadium slag composition design

Table 3: Designed slag formulations (g)

ID	Fe_2O_3	SiO_2	TiO_2	V_2O_5	Al_2O_3	Cr_2O_3	MgO	Al
S0	55	15	10	10	4	3	3	12.5
F1	32	15	10	10	4	3	3	
F2	35	15	10	10	4	3	3	
F3	37	15	10	10	4	3	3	
F4	40	15	10	10	4	3	3	
F5	45	15	10	10	4	3	3	
F6	50	15	10	10	4	3	3	
A1	55	15	10	10	4	3	3	
A2	55	15	10	10	6	3	3	
A3	55	15	10	10	8	3	3	
A4	55	15	10	10	10	3	3	
A5	55	15	10	10	15	3	3	
A6	55	15	10	10	20	3	3	
M1	55	15	10	10	4	3	8	
M2	55	15	10	10	4	3	10	
M3	55	15	10	10	4	3	12	
M4	55	15	10	10	4	3	15	
M5	55	15	10	10	4	3	20	
M6	55	15	10	10	4	3	25	

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 Fe_2O_3, Al_2O_3, 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 Fe_2O_3, Al_2O_3, 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 Fe_2O_3 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 Fe_2O_3 content, showing a positive correlation. The maximum precipitation amount is achieved with a Fe_2O_3 content of 50 %, reaching 30.82 %. This indicates a significant influence of the Fe_2O_3 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 FeV_2O_4 and $FeAl_2O_4$ constitute the highest proportion in the SP-V phase. With an increase in the Fe_2O_3 content, the proportion of MgV_2O_4 spinel in the SP-V phase initially increases and then decreases. When the Fe_2O_3 content is between 37 and 40 %, the proportion of MgV_2O_4 spinel in the SP-V phase reaches its maximum value of 15 %. Meanwhile, the proportion of FeV_2O_4 spinel in the SP-V phase decreases with the increase in the Fe_2O_3 content, declining from 48 to 34 %. The increased proportion of MgV_2O_4 spinel is attributed to the decreased proportion of FeV_2O_4 spinel. The proportion of $FeAl_2O_4$ also follows the pattern of initial decreasing and then increasing. As previously analyzed, under certain temperatures, FeV_2O_4 is more stable than $FeAl_2O_4$. FeV_2O_4 and MgV_2O_4 spinels are preferable solid chromium phases. Therefore, maintaining Fe_2O_3 at 37–40 % (minimizing the proportion of $FeAl_2O_4$) is conducive to the precipitation of vanadium in the form of FeV_2O_4 spinel. As indicated in **Figure 6b**, an increase in the Al_2O_3 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 Al_2O_3 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 Al_2O_3

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 Al_2O_3 content, the proportions of FeV_2O_4 and MgV_2O_4 spinels in the SP-V phase after solidification remain relatively unchanged. This implies that the changes in the Al_2O_3 content have a minimal impact on the proportions of various spinels in the SP-V phase. According to **Figure 6c**, when the 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 MgO content promotes the formation of the SP-V phase. Thus, maintaning the 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 MgO content, the proportion of MgV_2O_4 spinel in the spinel phase increases from 12 % to 25 %, while the proportion of FeV_2O_4 spinel decreases from 39 % to 26 %. This implies that an increased MgO content favors the enrichment of vanadium in the form of MgV_2O_4 spinel. Additionally, the content and proportion of $MgAl_2O_4$ spinel will also experience a substantial increase. In conclusion, a higher MgO content promotes the precipitation of MgV_2O_4 while inhibiting the precipitation of FeV_2O_4, making MgO an effective regulator of the composition of the SP-V phase.

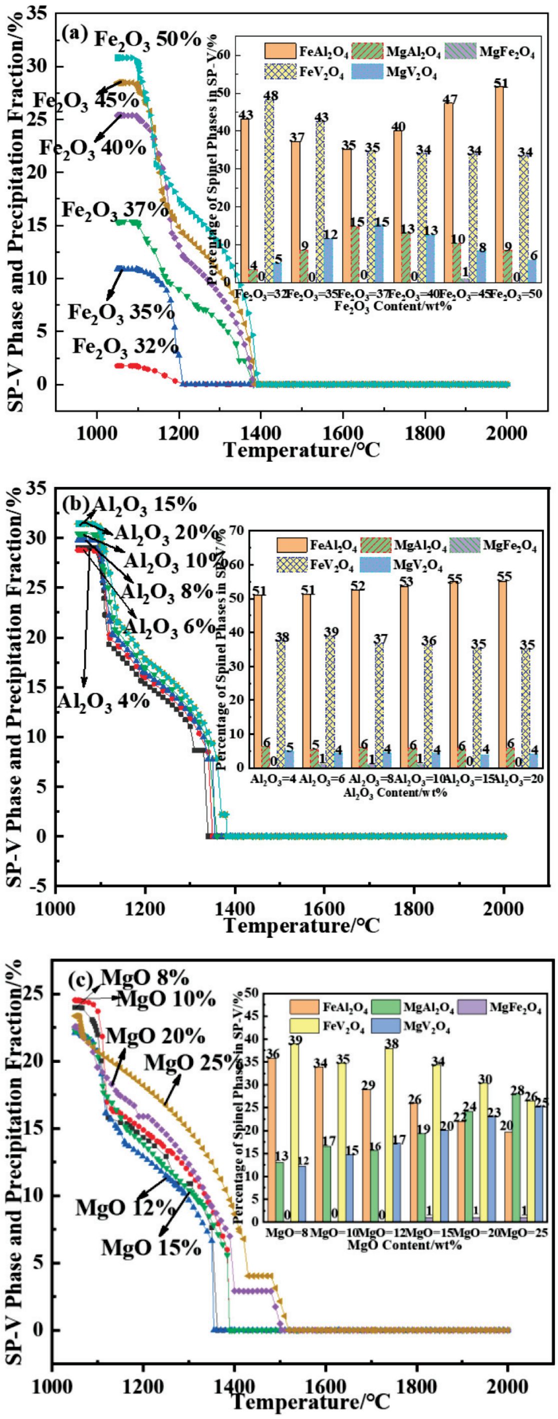

Figure 6: Influence of Fe_2O_3, Al_2O_3, and MgO contents on crystallization of the SP-V phase: a) effect of Fe_2O_3 on SP-V phase, b) effect of Al_2O_3 on SP-V phase, c) effect of MgO on SP-V phase

3.6 Fe_2O_3, Al_2O_3, and MgO content effects on FeV_2O_4 and MgV_2O_4 spinel phase precipitation in slag

The influences of Fe_2O_3, Al_2O_3, and MgO contents on the precipitation behavior of FeV_2O_4 and MgV_2O_4 spinel phases in the slag are depicted in **Figure 7**. As shown in **Figure 7a**, the precipitation fraction of the FeV_2O_4 spinel phase in the slag increases with a higher Fe_2O_3 content. When the Fe_2O_3 content reaches 50 %, the precipitation fraction of the FeV_2O_4 spinel phase reaches its maximum value of 9.668 %. This is due to a substantial reduction of Fe_2O_3 to FeO in the slag, leading to the reaction of FeO with V_2O_3 to form the FeV_2O_4 spinel phase. An increased FeO content enhances the enrichment of the SP-V phase, further increasing the precipitation of the FeV_2O_4 spinel phase. According to the figure, the precipitation fraction of the MgV_2O_4 spinel phase initially increases and then decreases with the rising Fe_2O_3 content. The MgV_2O_4 spinel phase content increases from 0.08 % to 3.06 % as the Fe_2O_3 content rises to 40 %, and then decreases to 1.72 % with further increases in the Fe_2O_3 content. This suggests that the addition of Fe_2O_3 generally promotes the precipitation of the SP-V phase, especially the main component FeV_2O_4, and controlling the Fe_2O_3 mass fraction within a range of 40–50 % is favorable for the precipitation of the FeV_2O_4 spinel phase and enrichment of vanadium in the spinel phase. Consequently, it can be inferred that the FeO content is also a crucial factor influencing vanadium extraction in the slag system.

As illustrated in **Figure 7b**, the precipitation fraction of the FeV_2O_4 spinel phase increases with a higher Al_2O_3 content, showing a positive correlation. When the Al_2O_3 content reaches 20 %, the precipitation fraction of the FeV_2O_4 spinel phase reaches its maximum value of 10.347 %. This is attributed to Al_2O_3 promoting the generation of FeO, leading to an increase in the FeO content

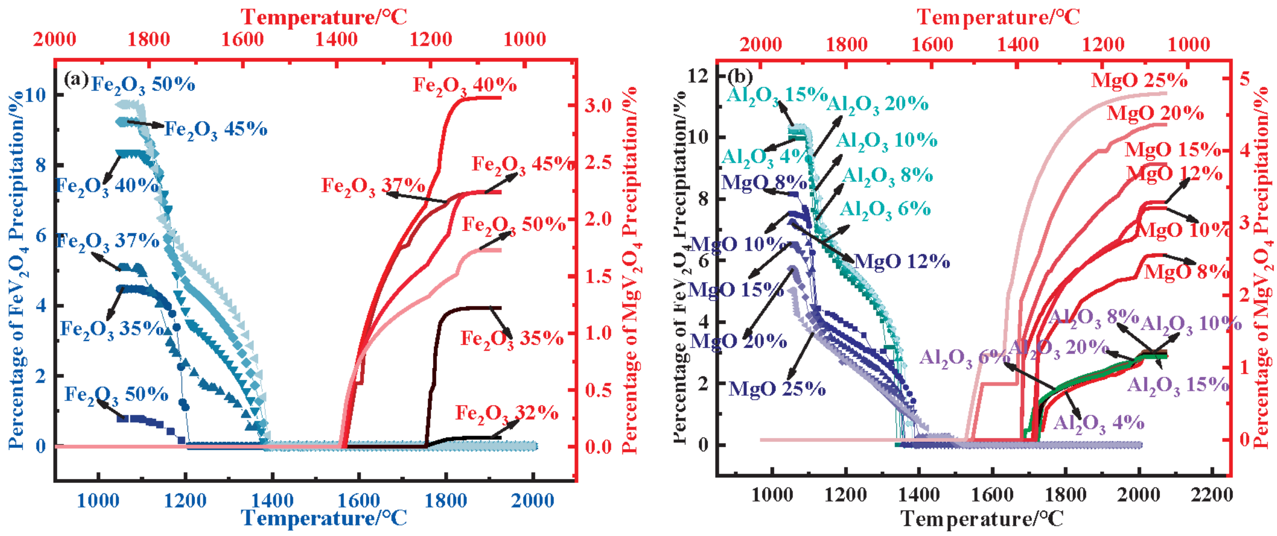

Figure 7: Influences of Fe_2O_3, Al_2O_3, and MgO contents on the precipitation of the SP-V phase: a) Effects of Fe_2O_3 on FeV_2O_4 and MgV_2O_4, b) effects of Al_2O_3 and MgO on FeV_2O_4 and MgV_2O_4, respectively

in the slag, and subsequently enhancing the precipitation of the FeV_2O_4 spinel phase. The content of the MgV_2O_4 spinel phase increases and then decreases with the rising Al_2O_3 content. When the Al_2O_3 content increases to 8 %, the MgV_2O_4 spinel phase content increases from the original 1.15 to 1.23 %. Overall, the addition of Al_2O_3 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 FeV_2O_4 increases while its precipitation fraction decreases, showing an inverse relationship. When the addition of MgO increases from 8 to 25 %, the precipitation temperature of FeV_2O_4 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 MgV_2O_4 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 MgV_2O_4 is considerable. At 1150 °C, when the MgO addition increases from 8 % to 25 %, the precipitation fraction of MgV_2O_4 increases from 2.55 % to 4.79 %, which is a moderate increase. Therefore, the promotion of MgV_2O_4 spinel precipitation by MgO comes at the expense of a reduction in the FeV_2O_4 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 FeV_2O_4 and MgV_2O_4 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 MgV_2O_4 and FeV_2O_4 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 $MgCr_2O_4$ and $FeCr_2O_4$ 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 $Al_4FeSi_5O_{18}$, $Al_4MgSi_5O_{18}$, and spinel phases. The SP-V phase predominantly comprises MgV_2O_4 and FeV_2O_4, while the SPINA phase is primarily composed of $MgCr_2O_4$ and $FeCr_2O_4$.In general, the Fe_2O_3 content significantly affects the precipitation behavior of the SP-V phase. A moderate increase in Fe_2O_3 promotes the precipitation of FeV_2O_4 and MgV_2O_4. However, excessive Fe_2O_3 suppresses the precipitation of MgV_2O_4. The Al_2O_3 content influences the overall precipitation of the SP-V phase, with a moderate Al_2O_3 content facilitating the precipitation of FeV_2O_4 spinel, especially at an Al_2O_3 content of 20 %, where the precipitation rate of FeV_2O_4 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 MgV_2O_4 rises, while that of FeV_2O_4 decreases. Controlling the MgO content at around 20 % is advantageous for the enrichment of vanadium in the form of both FeV_2O_4 and MgV_2O_4 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

The authors gratefully acknowledge the support of the Postgraduate Innovation Project of North China University of Science and Technology (2024S11), the Central-Guided Local Science and Technology Development Funding Project of Hebei Province (236Z3803G), and the Science and Technology Plan Project of Tangshan City (23130205E).

5 REFERENCES

[1] J. Wen, T. Jiang, M. Zhou, H. Gao, J. Liu, X. Xue, Roasting and leaching behaviors of vanadium and chromium in calcification roasting–acid leaching of high-chromium vanadium slag, Int. J. Miner. Metall. Mater., 25 (**2018**), 515–526, doi:10.1007/s12613-018-1598-3

[2] S. Zhang, G. Li, R. Xiao, Extraction of vanadium from low-vanadium grade magnetite concentrate pellets with sodium salt, Journal of Materials Research and Technology, 15 (**2021**), doi:10.1016/j.jmrt.2021.11.039

[3] J. Xiang, Q. Huang, X. Lv, C. Bai, Multistage utilization process for the gradient-recovery of V, Fe, and Ti from vanadium-bearing converter slag, Journal of Hazardous Materials, 336 (**2017**), 1–7, doi:10.1016/j.jhazmat.2017.04.060

[4] Z. Tong, J. Fan, Q. Zeng, Z. Jia, X. Lin, Research status and prospect of preparation of foam glass ceramics from metal tailings, Nonferrous Metals Science and Engineering, 11 (**2020**) 3,4–41, doi:10.13264/j.cnki.ysjskx.2020.02.005

[5] X. Huo, X. Zhang, Z. Ding, A clean approach for detoxification of industrial chromium-bearing stainless steel slag: Selective crystallization control and binary basicity effect, Journal of Hazardous Materials, 446 (**2023**), 130746, doi:10.1016/j.jhazmat.2023.130746

[6] Z. Tong, Z. Jia, Q. Zeng, C. Xu, Q. Zeng, Thermodynamics of the effects of slag compositions on the precipitation of chromium spinel in $CaO-MgO-Al_2O_3-SiO_2-Cr_2O_3-FeO-TiO_2$ slag system, Nonferrous Metals Science and Engineering, 11 (**2020**), 1–10, doi:10.13264/j.cnki.ysjskx.2020.03.001

[7] O. I. Ostrovski, Y. I. Utochkin, A. V. Pavlov, R. A. Akberdin, Viscosity of the $CaO-CaF_2$ System Containing Chromium Oxide, Transactions of the Iron & Steel Institute of Japan, 34 (**1994**), 773–775, doi:10.2355/isijinternational.34(1994).773

[8] Q. Li, J. Gao, Y. Zhang, Z. An, Z. Guo, Viscosity measurement and structure analysis of Cr_2O_3-bearing $CaO-SiO_2-MgO-Al_2O_3$ slags, Metallurgical and Materials Transactions B, 48 (**2017**), 346–356, doi:10.1007/s11663-016-0858-8

[9] W. Xie, Phase structure, phase equilibria and thermodynamic properties in iron-vanadium oxides, Doctoral dissertation, University of Science and Technology Beijing, 2020, doi:10.26945/d.cnki.gbjku.2020.000135

[10] W. Du, Fundamental Research of Thermodynamic Optimization of Fe-V-Si-O System and CO2 Used in Vanadium-Extraction Process, Doctoral dissertation, Chongqing University, 2019, doi:10.27670/d.cnki.gcqdu.2019.003208

[11] R. Gilligan, The extraction of vanadium from titanomagnetites and other sources, Miner. Eng, 146 (**2020**), doi:10.1016/j.mineng.2019.106106

[12] D. Huang, Vanadium refining in steelmaking, Metallurgical Industry Press, Beijing 2000, 3–4

[13] L. Su, J. Xu, L. Zuo, Thermodynamic calculation of precipitation behavior of chromium spinel in the $CaO-SiO_2-MgO-Al_2O_3-FeO-Cr_2O_3$ slag system, Nonferrous Metals Science and Engineering, 14 (**2023**), 302–310, doi:10.13264/j.cnki.ysjskx.2023.03.002

[14] H.-Y. Li, H.-X. Fang, K. Wang, W. Zhou, Z. Yang, X.-M. Yan, W.-S. Ge, Q.-W. Li, B. Xie, Asynchronous extraction of vanadium and chromium from vanadium slag by stepwise sodium roasting–water leaching, Hydrometallurgy, 156 (**2015**), 124–135, doi:10.1016/j.hydromet.2015.06.003

[15] X. Li, Kinetic of Isothermal Growth of Spinel in Vanadium Slag, Chinese Journal of Rare Metals, 35 (**2011**), 281–285, doi:10.3969/j.issn.0258-7076.2011.02.023

[16] C. Pan, Study on the Precipitation Behavior and Control of Titanium-Containing Inclusions in 321 Stainless Steel, Doctoral dissertation, University of Science and Technology Beijing, 2021, doi:10.26945/d.cnki.gbjku.2021.000116

[17] A. Tang, K. Huang, J. Zhao, Electrochemistrical Performance of Spinel LiMn2O4 Cathode Material for Lithium Ion Battery at Elevate Temperature, Fine Chemical Intermediates, 32 (**2002**), 35–37, doi:10.19342/j.cnki.issn.1009-9212.2002.04.014

[18] Z. Dong, Fundamental study on co-extraction and separation of vanadium, titanium and chromium from vanadium slag, Doctoral dissertation, University of Science and Technology Beijing, 2022, doi:10.26945/d.cnki.gbjku.2022.000265

[19] R. L. Howard, S. R. Richards, B. J. Welch, J. J. Moore, Vanadium distribution in melts intermediate to ferroalloy production from vanadiferous slag, Metallurgical and Materials Transactions B, 25 (**1994**), 27–32, doi:10.1007/BF02663175

[20] H. Wang, G. Li, B. Li, X. Zhang, Y. Yan, Effect of B_2O_3 on Melting Temperature of CaO-Based Ladle Refining Slag, Journal of Iron and Steel Research International, 17 (**2010**), 18–22, doi:10.1016/S1006-706X(10)60177-X

[21] F. Engström, D. Adolfsson, Q. Yang, C. Samuelsson, B. Björkman, Crystallization Behaviour of some Steelmaking Slags, Steel Research International, 81 (**2010**), 362–371, doi:10.1002/srin.200900154

[22] W. Li, X. Xue, Effect of cooling regime on phase transformation and chromium enrichment in stainless-steel slag, Ironmak. Steelmak., 46 (**2019**), 642–648, doi:10.1080/03019233.2018.1436890

[23] H.-X. Fang, H.-Y. Li, X. Li, B. Xie, Sodium Roasting Thermodynamics of Chromium-Containing Vanadium Slag and Its Application, Rare Metal Technology, John Wiley & Sons, Inc, Hoboken, NY, USA, 2014, 189–195, doi:10.1002/9781118888551.ch34

[24] N. Wang, Z. Zou, Z. Zhang, Y. Xiao, Y. Yang, Thermodynamics of Slag Formation in Multi-Component Oxide Systems in Thermal Processing of Incineration Bottom Ash - Equilibrium Phase Relation in $CaO-SiO_2-FeO_x-MgO$ System, Advanced Materials Research, (**2011**) 194–196, 2175–2178, doi:10.4028/www.scientific.net/AMR.194-196.2175

[25] Y. Zhou, Theory and Technology of Making High Speed Steel by Direct Alloying of Tungsten Molybdenum Vanadium Oxide Ore, China Tungsten Industry, 21 (**2006**), 13–18, doi:10.3969/j.issn.1009-0622.2006.01.005

[26] D. Sun, Thermodynamic analysis on the oxidation of the elements from low vanadium molten iron, Journal of Inner Mongolia University of Science and Technology, 33 (**2014**), 140–144, doi:10.7666/d.D517089

[27] Y. Yu, Thermodynamic calculation of FeO effect on precipitation of spinel containing chromium in CaO-SiO2-MgO-Al2O3-Cr2O3 system, Journal of Wuhan University of Science and Technology (Natural Science Edition), 41 (**2018**), 15–19, doi:10.3969/j.issn.1674-3644.2018.01.003

[28] Y. Jeong, M. Fan, S. Singh, C.-L. Chuang, B. Saha, J. Hans Van Leeuwen, Evaluation of iron oxide and aluminum oxide as potential arsenic(V) adsorbents, Chemical Engineering and Processing – Process Intensification, 46 (**2007**), 1030–1039, doi:10.1016/j.cep.2007.05.004