Industrial Application of Large Rotary Kiln for Recovery of Vanadium from Vanadium Slag Added MnVO$_4$ in Calcium Roasting Process

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Calcification roasting was an effective and environment-friendly way to extract vanadium from vanadium slag. This paper presents a comprehensive study on industrial application of calcium roasting process for large rotary kiln. The study has highlighted the importance of temperature stability using MnVO$_4$ for maximizing the recovery of the vanadium. The optimum conditions for recovering 87.48–89.65% of vanadium (V) by using MnVO$_4$ at M·Fe concentration ±0.5%, CaO to V$_2$O$_5$ ratio 0.58–0.64, MnVO$_4$ concentration 50–55%, feed rate 4.44±0.56 kg/s, rotate speed 87–90 s/r, temperature of T2 865±10°C, temperature control curves TE, TF, TG, negative pressure −10±5 Pa and volume flow ratio of the combustion air to coke oven gas (5–5.5). It was possible MnVO$_4$ was not only the additive but also play a key auxiliary effect for CaO with vanadium (V) to Ca$_2$V$_2$O$_7$ by studying on the oxidation reaction mechanism.

KEY WORDS: vanadium slag; calcification roasting; large rotary kiln; MnVO$_4$; oxidation reaction mechanism.

1. Introduction

Recycling of waste material has become very important during the past decade due to the reinforcement of environmental protection laws and regulations that require minimizing the waste disposal. Steelmaking operations are special concerned by this problem due to the production of a huge quantity of by-products such as vanadium slag.$^{1-5}$ The extensive of vanadium product (V$_2$O$_3$, V$_2$O$_5$, FeV$_5$O$_9$, FeV$_8$O$_9$: vanadium content not less than 50% and 80% from GB4139-87) and vanadium nitride alloys in metalurgical, chemical, aviation, medical, iron and steel, and other industries have increasing attentions due to its high tensile strength, hardness and fatigue resistance of special chemical activity and physical properties.$^{6-11}$ Vanadium resource is abundant in vanadium-titanium magnetite ore in Panxi area of China and the steelmaking vanadium slag not only occupies plenty of land but also increases the disposal costs. Therefore, recycling of vanadium from steelmaking vanadium slag has become very important due to the reinforcement of environmental regulations that require the minimum discharge to reduce environmental pollution and health hazards.

Vanadium slag is mainly treated by means of two processes for sodium salts roast-water leaching and calcification roast-acid leaching. However, Sodium salts roast-water leaching method with one or combination of NaCl, Na$_2$CO$_3$, and Na$_2$SO$_4$ as additive followed by water leaching has several disadvantages such as high production, leaching residue, solid waste Na$_2$SO$_4$, wastewater treatment costs, complicated processes, the emission of corrosive gas HCl, Cl$_2$, SO$_2$ and SO$_3$, low vanadium oxidation ratio 82–86% and fusion agglomeration at temperature for low melting point of sodium salts, low CaO in vanadium slag requirements$^{12-19}$ and limit further application of this technology.

In order to cope with these disadvantages, calcification roasting-acid leaching is an alternative to sodium salts roasting-water leaching.$^{20}$ Instead of sodium salts, lime or limestone are used as additives during roasting process to product calcium vanadium, including CaV$_2$O$_6$, Ca$_2$V$_2$O$_7$, and Ca$_3$V$_2$O$_8$ and followed by sulphuric acid leaching to obtain vanadium solution. Calcification roasting-acid leaching was first used in Tula plant in Russia and vanadium products factory of Xichang steel vanadium co., LTD in China due to the cleaner production process.

Therefore, a new type of additive MnVO$_4$ was the first used in the calcium roasting in the large rotary kiln to explore the optimal process operating parameters in this paper. Roasting conditions, including M·Fe concentration, CaO to V$_2$O$_3$ ratio (CaO/V$_2$O$_3$), MnVO$_4$ concentration, feed rate, rotate speed, temperature distribution, negative pressure and volume flow ratio of the air to the coke oven gas, were optimized.
2. Experimental

2.1. Materials

The vanadium slag studied in this paper was produced in steelmaking plant of Pan steel Group Xichang Steel and Vanadium Company (Sichuan Province, China). The vanadium slag was smashed, milled and wiped off magnetic material (M·Fe) that is magnetized by the NS magnet. The chemical composition and particle size distribution of vanadium slag was analyzed by X-ray fluorescence as shown in Table 1, where −80 mesh, +120 mesh, −160 mesh, −240 mesh stand for 0.180 mm, 0.120 mm, 0.096 mm, 0.061 mm in plus sieve or undersize. The CaO/V₂O₅ ratio in vanadium slag is about 0.117. The property of vanadium slag and limestone was shown in Tables 2 and 3. The MnVO₄ was self-production.

2.2. Industrialization Experimental Setup

A schematic diagram of the industrialization experimental apparatus is presented in Fig. 1. In Fig. 1, a large rotary kiln has 3.6 m outer diameter (Do), 3.1 m inner diameter (Di) and 90 m length (L) with the angle of 5°. The solid inlet is mixture consist of fine vanadium slag, limestone and MnVO₄. The solid outlet is clinker using acid leaching to obtain conversion rate of vanadium. The gas inlet is gas phase consist of combustion-supporting air, oxygen, coke oven gas which mix in burner to burn for quantity of heat. The six thermocouples of T1, T2, T3, T4, T5 and T6 were 3 m, 13 m, 23 m, 33 m, 48 m and 73 m length (L1, L2, L3, L4, L5 and L6) which is apart from the head of rotary kiln.

2.3. Procedure

2.3.1. Calcification Roasting

Calcification roasting was done to change vanadium compound to acid soluble form vanadium. Limestone, MnVO₄ with vanadium slag were mixed in the certain mass ratio and CaO/V₂O₅ ratio in mixing motor for 3–5 min. The mixture was roasted in (Ф3.6×90 m) rotary kiln at the following conditions shown in Table 4.

2.3.2. Acid Leaching

The roasted vanadium slag was leached by sulphuric acid at certain temperature, pH, acid concentration, liquid/solid ratio, agitation speed and time. A schematic diagram of acid leaching and acid soluble form vanadium V⁵⁺ analysis is presented in Fig. 2. In specific volume beaker (500 mL), 10 g of finely grinded 0.096 mm (−160 mesh) calcification clinker mixed with 250 mL deionized water (pH=6.65). The reaction mixture was stirred with digital stirring motor (Type JJ-1A, Jintan Instrument manufacturing co., LTD, China) at 6.67–7.50 r/s and heated in digital thermostat water bath pot (Type HH-2, Jintan Experimental Instrument factory, China) at 45°C for 60 min. The sulphuric acid (0.62×10⁻² mol/L) is added drop wise to mixture keep the pH for 2.8±0.1 by pH meter (HI 2223 calibration check, HANNA instruments). After leaching the grinded mixture at 2.8±0.1 pH for 60 min, the mixture was filtrated using circulating water multi-purpose vacuum pump (Type SHB-3, Zhenzhou Mechanical Equipment Corp., China) at 0.05 MPa and washed several times using the dilute sulphuric acid water (pH=2.8). The residue is baked at 105°C for

<table>
<thead>
<tr>
<th>Table 1. The Chemical composition of vanadium slag studied before the removal of M·Fe.</th>
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<th></th>
<th></th>
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<tr>
<td>Compound</td>
<td>V₂O₅</td>
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<td>SiO₂</td>
<td>CaO</td>
<td>MnO</td>
<td>Cr₂O₃</td>
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<td>mass%</td>
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<td>11.30</td>
<td>14.52</td>
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<td>CaO</td>
<td>M·Fe</td>
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<tr>
<td>mass%</td>
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<td>2.42</td>
<td>0.1</td>
<td>97.5</td>
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<th>Table 4. Experimental conditions.</th>
<th></th>
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<tbody>
<tr>
<td>Process parameters</td>
<td>Values</td>
</tr>
<tr>
<td>M·Fe content of fine vanadium slag [mass%]</td>
<td>0–6%</td>
</tr>
<tr>
<td>MnVO₄ concentration in mixture [mass%]</td>
<td>0–57.5%</td>
</tr>
<tr>
<td>CaO/V₂O₅ ratio in mixture [kg/kg]</td>
<td>0.3–1.0</td>
</tr>
<tr>
<td>Feed rate of the rotary kiln</td>
<td>1.67–5.56 kg/s</td>
</tr>
<tr>
<td>Rotating rate of the rotary kiln</td>
<td>87–113 s/r</td>
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<tr>
<td>The length of the rotary kiln</td>
<td>90 m</td>
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<tr>
<td>The outer diameter of the rotary kiln (Do)</td>
<td>3.6 m</td>
</tr>
<tr>
<td>The inner diameter of the rotary kiln (Di)</td>
<td>3.1 m</td>
</tr>
<tr>
<td>Gas phase</td>
<td>air, oxygen, coke oven gas</td>
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<td>Solid phase</td>
<td>vanadium slag, limestone, MnVO₄</td>
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<tr>
<td>Temperature of T2</td>
<td>830–910°C</td>
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Fig. 1. Schematic diagram of the vanadium slag large-scale (Ф3.6×90 m) rotary kiln calcium roasting system. (Online version in color.)

Fig. 2. Schematic diagram of acid leaching and acid soluble [V⁵⁺] analysis.
2.3.3. Analytical Method

Analytical method was called QJ/XC5.251-2014. Cooling the residue at room temperature for 30 min, 0.25 g of finely ground calcination roasted clinker and leaching residue was used to detect the total amount of vanadium [T-V] by NH₄HSO₄ oxidation and [(NH₄)₂Fe(SO₄)₂·6H₂O] titration method. The acid soluble [V⁵⁺] concentration in the calcination clinker is calculated by the mass M and [T-V] of clinker and residue from mass balance 

\[
\frac{[V^{5+}]_{\text{clinker}}}{[T-V]_{\text{clinker}}} = \frac{M_{\text{clinker}} - M_{\text{residue}}}{[T-V]_{\text{residue}}} \times 100\%.
\]

Where [V⁵⁺]_{\text{clinker}} and [T-V]_{\text{clinker}} stand for acid soluble vanadium concentration and the total vanadium concentration in clinker which roasting in rotary kiln, respectively. Reproducibility was confirmed as ±2% or better.

3. Experimental Results for Optimization of Process Parameters

The results of the effect of M·Fe concentration 0–6%, CaO/V₂O₅ ratio 0.3–1.0, MnVO₄ concentration 0–57.5%, feed rate 1.67–5.56 kg/s, Mn VO₄ concentration in mixture 50%, rotate speed of rotary kiln 90 s/r, temperature of T2 870±5°C at the length of rotary kiln 13 m, negative pressure of the head of rotary kiln −10±5 Pa, volume flow ratio of the air to coke oven gas 5.5.

3.1. Effect of M·Fe Concentration in Fine Vanadium Slag

The effect of M·Fe concentration in fine vanadium slag on the conversion rate of vanadium was investigated. The operating parameters were: feed rate of mixture 2.22±0.14 kg/s, Mn VO₄ concentration in mixture 50%, temperature of T2 870±5°C at the length of rotary kiln 13 m, negative pressure of the head of rotary kiln −10±5 Pa, volume flow ratio of the air to coke oven gas 5.5.

3.2. Effect of CaO to V₂O₅ Ratio in Mixture

The effect of CaO to V₂O₅ ratio in mixture on conversion rate of vanadium is illustrated in Fig. 3. It can be seen that the vanadium conversion rate increases with the CaO to V₂O₅ ratio, and then slightly decreases when it is above 0.64. As the CaO to V₂O₅ ratio increases further above 0.75, this effect disappears. According to the obtain result, it can be concluded that the CaO to V₂O₅ ratio of 0.58–0.64 is the best for vanadium conversion rate of 90.58–92.20%. The result is supported by W. C. Song et al. An increase in the CaO content leads to an increase in the formation of Ca₂V₂O₇ due to the fact that CaO may stabilize the higher valence state of vanadium.

3.3. Effect of MnVO₄ Concentration in Mixture

MnVO₄ was the first used in the calcium roasting in...
the large rotary kiln. The effect of MnVO₄ concentration on conversion rate of vanadium was investigated in wide concentration range of 0–57.5%. As shown in Fig. 5, the conversion rate increased sharply and kept high conversion rate of 89.95–91.42% at MnVO₄ concentration 50–55%. When MnVO₄ concentration from 50% to 57.5%, the conversion rate passed 88% and kept constant. From this result, 50–55% concentration of the MnVO₄ was selected, which was enough to stabilize the temperature control curve and kept high conversion rate.

3.4. Effect of Feed Rate of Mixture on Conversion Rate of Vanadium

The influence of feed rate of mixture on conversion rate of vanadium at M·Fe concentration 1 ± 0.5%, CaO to V₂O₅ ratio of 0.58–0.64, MnVO₄ concentration in mixture 50–55%, rotate speed of rotary kiln 87–90 s/r, temperature T2 of 870 ± 5°C at the length of rotary kiln 13 m, negative pressure of the head of rotary kiln −10±5 Pa and volume flow ratio of the air to coke oven gas 5.5 as shown in Fig. 6. It was clear that the conversion rate of vanadium decreased slightly in the range of 1.67–5.56 kg/s, the conversion rate of vanadium remained nearly constant above 88%. Therefore, the feed rate 4.44±0.56 kg/s was selected due to feed rate 1.67–3.89 kg/s not demand the product quality and 5.00–5.56 kg/s not demand the temperature control curve of connecting T1, T2, T3, T4, T5 and T6.

3.5. Effect of Rotate Speed of the Rotary Kiln on Conversion Rate

The influence of rotate rate of rotary kiln on conversation rate at M·Fe concentration 1 ± 0.5%, CaO to V₂O₅ ratio of 0.58–0.64, MnVO₄ concentration in mixture 50–55%, feed rate of mixture 4.44±0.14 kg/s, temperature T2 of 870±5°C at the length of rotary kiln 13 m, negative pressure of the head of rotary kiln −10±5 Pa, volume flow ratio of the air to coke oven gas 5.5 as shown in Table 5. Therefore, 87 s/r rotate rate of rotary kiln was selected.

3.6. Effect of Reaction Temperature on Conversion Rate of Vanadium

It was observed that the main reaction temperature of T2 and temperature control curve of connecting T1, T2, T3, T4, T5 and T6 also played a key role on conversion rate of vanadium. Main reaction temperature of T2 was optimized in the range of 830–910°C. The experimental conditions were kept constant at M·Fe concentration 1 ± 0.5%, CaO to V₂O₅ ratio of 0.58–0.64, MnVO₄ concentration in mixture 50–55%, feed rate of mixture 4.44±0.14 kg/s, rotate speed of rotary kiln 87 s/r, negative pressure of the head of rotary kiln −10±5 Pa, volume flow ratio of the air to coke oven gas 5.5. As shown from Fig. 7, conversion rate of vanadium increased sharply by increasing the reaction temperature from 830°C to 875°C was from 78.18% to 91.02%. When the reaction temperature increased from 875°C to 910°C, conversion rate of vanadium decreased slightly from 90.70% to 89.52% due to material surface sintering which hinders the diffusion of oxygen. In sake of energy saving, 865±10°C was the optimal main temperature of T2 for calcification roasting.

As shown from Table 6, TA, TB, TC, TD, TE, TF, TG temperature control curves of connecting T1, T2, T3, T4, T5 and T6 are different to obtain different vanadium conversion rate, T2 is high but T5 is low. But TE, TF, TG temperature control curves are perfectly, the conversion rate of vanadium is above 90%. Therefore, T2 for 865±10°C and temperature control curves TE, TF, TG are selected.
negative pressure has a significant effect on the oxidation of vanadium and maximum extraction was achieved for negative pressure of the head of rotary kiln $-10 \pm 5$ Pa.

3.8. Effect of Volume Flow Ratio of the Air to Coke Oven Gas on Conversion Rate of Vanadium

Figure 9 shows the effect of volume flow ratio of the air to coke oven gas on conversion rate of vanadium at $M \cdot Fe$ concentration $1 \pm 0.5\%$, CaO to $V_2O_5$ ratio of $0.58–0.64$, Mn$VO_4$ concentration in mixture $50–55\%$, feed rate of mixture $4.44 \pm 0.14$ kg/s, rotate speed of rotary kiln $87$ s/r, temperature of $T_2 865 \pm 10^\circ C$, negative pressure of the head of rotary kiln $-10 \pm 5$ Pa.

4. Discussion

4.1. Optimum Temperature Condition for Recover of Vanadium

Temperature conditions including master temperature point of $T_2$ and optimal temperature control curves of connecting $T_1$, $T_2$, $T_3$, $T_4$, $T_5$ and $T_6$ are selected in section 3.6 as shown in Fig. 7 and Table 6. Master temperature point of $T_2$ which is closest to the flame and can represent the highest temperature in the kiln is higher than $900^\circ C$ due to the high temperature, the formation of liquid phase sintering, calcification roasted clinker is hard and vanadium conversion rate decreases by $2–3\%$. Master temperature point of $T_2$ is low than $850^\circ C$ due to the low temperature and incomplete roasting, calcification roasted clinker vanadium conversion rate decreases by $3–5\%$. But just controlling temperature point of $T_2$ is not enough, temperature control curves of connecting $T_1$, $T_2$, $T_3$, $T_4$, $T_5$ and $T_6$ that change with above operation factors shown in Section 3 are controlled at the core of the kiln temperature control. The optimal temperature curve and temperature inversion curve occur in two different stages of production as shown in Fig. 10. First production stage, vanadium plant was put into operation before December 2013. However, the temperature control curve of the rotary kiln did not reach the process requirements, mainly in the $T_3$, $T_4$, $T_5$ tempera-
ture was abnormally high. Especially, T3 and T4 average temperature reached 934°C and 914°C, far more than the normal maximum roasting temperature 880°C, which was the main reason of sticking material of kiln and too hard ball firing. T6 temperature decreased by 100°C and basically stable because of material was heated before feeding at 560°C and after feeding. T4 temperature that arrived at feeding 2.5 h increased sharply in a short period of time and T5 temperature was also changing a similar trend caused by heat. Roasting temperature appeared “upside down” phenomenon compared with the optimal temperature curve. Although a large number of temporary measures had been taken to close the optimal temperature curve, such as reducing the gas flow rate, reducing the negative pressure of the kiln head and so on, it had not been solved and so many times stop kiln processing kiln sintering material.

And after cooling treatment to ensure the roasting effect, it many times stop kiln processing kiln sintering material. Of the factors that affected the temperature stability have discussion with Table 6, Table 7 and production experiences. The discussion as follows:

(1) M-Fe concentration above 1.5% has significant effect on the temperature stability in calcium roasting process because of fast exothermic reaction such as Fe+\(\text{O}^2\)=FeO, \(2\text{Fe}+3\text{O}^2\)=Fe\(_2\)O\(_4\), \(3\text{Fe}+4\text{O}^2\)=FeO\(_4\). It is typical of magnetothermal oxidation and exothermic reaction of metal iron. Although magnetism is not all metal iron, it is obvious that magnetic material is heated during roasting, especially above high temperature of 800°C will produce larger heat cause serious ring and the control of roasting temperature is very influential. Moreover, in clinker containing vanadium acid leaching process, the metal iron partly dissolved and reductive yellow \(V^5\) to blue \(V^4\) in solution, solution dissolve out a large number of iron ions, cause a reaction of the electrolyte solution, solution black color overlay.

(2) CaO/V\(_2\)O\(_3\) ratio is calculated by the mass and element of \(V\) and \(Ca\) in CaCO\(_3\) and vanadium slag. Calcium oxide is the most important reagent for roasting. Vanadium spinel (FeV\(_2\)O\(_4\)) in the inner was oxidized to V\(_2\)O\(_3\) at 210–660°C and reacted with calcium oxide decomposed by CaCO\(_3\) at 550–700°C. Calcium vanadate Ca(VO\(_3\))\(_2\), \(Ca_2V_2O_7\), \(Ca_3(VO_4)_2\) were produced at different theoretical CaO/V\(_2\)O\(_3\) ratio of 0.31, 0.63, 0.92 and different roasting temperature at 600–880°C as shown in below: \(^{23}\)

\[
4\text{FeV}_2\text{O}_4 + 5\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{V}_2\text{O}_3 \quad \text{(2)}
\]

\[
\text{CaO} + \text{V}_2\text{O}_3 = \text{Ca}(\text{VO}_3)_2 \quad \text{(3)}
\]

\[
2\text{CaO} + \text{V}_2\text{O}_3 = \text{Ca}_2\text{V}_2\text{O}_7 \quad \text{(4)}
\]

\[
3\text{CaO} + \text{V}_2\text{O}_3 = \text{Ca}_3(\text{VO}_4)_2 \quad \text{(5)}
\]

Major vanadate \(Ca_2V_2O_7\) can be easy to leach with sulfuric acid because of theoretical CaO/V\(_2\)O\(_3\) ratio of 0.45–0.63 while Ca(VO\(_3\))\(_2\), \(Ca_3(VO_4)_2\) was hard to leach due to its low content and poor crystallinity. \(^{23}\) The lower the CaO/V\(_2\)O\(_3\) ratio of low limestone and more vanadium slag, the higher the roasting temperature for feeding temperature between T6 and T5. The higher the CaO/V\(_2\)O\(_3\) ratio of more
limestone and low vanadium slag, the lower the roasting temperature for feeding temperature between T6 and T5. Vanadium conversion rate change with CaO/V2O5 ratio and roasting temperature curve fluctuated greatly because of different calcification reaction.

(3) To increase the stability of temperature control curve and vanadium conversion rate, MnVO4 was added to the mixture of limestone and vanadium slag. The promoting effect of MnVO4 could be attributed to the Mn2O3 and V2O5 in MnVO4 which enhances oxidation interaction between elements and transports [O] through the catalytic action in roasting process.23–25)

\[
\text{FeV}_2\text{O}_4 + 1.5\text{Mn}_2\text{O}_3 + [\text{O}] = 0.5\text{Fe}_2\text{O}_3 + 2\text{V}_2\text{O}_3 + 3\text{MnO} \quad \ldots \ldots \ldots \ldots (6)
\]

\[
\text{FeV}_2\text{O}_4 + 1.5\text{V}_2\text{O}_3 = 0.5\text{Fe}_2\text{O}_3 + 2.5\text{V}_2\text{O}_4 \quad \ldots \ldots \ldots \ldots (7)
\]

In the process of roasting vanadium slag, most of the heat capacity comes from the oxidation of Fe, FeO and FeV2O4. Therefore, its chemical reaction heat is the main heat capacity comes from the oxidation of Fe, FeO and FeV2O4. Therefore, its chemical reaction heat is the main heat of MnVO4 concentration, feed rate, rotate speed, negative pressure and the volume of combustion air, coke oven gas, oxygen have significant interaction influence on temperature stability and vanadium conversion rate. So it is necessary to control these factors in order to ensure the stability of the rotary kiln, especially the stability of the temperature.

4.4. The Proper Mechanism of Adding Optimum MnVO4 and CaCO3 in FeV2O4

According to the above experiment data, discussion and reference23–25) the calcification roasting chemistry reaction mechanism of vanadium may be represented by the scheme shown in Fig. 11. The following steps are involved in transport process:

(1) Feed reaction section from inlet to T6 temperature have a cyclic oxidation-reduction reaction: MnVO4 that mainly contain Mn2O3 and V2O5 can react with FeV2O4 by oxidation-reduction reaction at 300–550°C and Mn, Fe, V elements valence change (Fe2+→Fe3+, Mn2+→Mn2+, V3+→V5+→V7+), produce MnO and V2O4 sharply is oxidized and recombine into MnVO4.

![Fig. 11](image_url)

**Fig. 11.** Scheme of the oxidation mechanism added MnVO4 in calcification roasting.

\[\text{Table 8. The effect of MnVO}_4\text{ and CaCO}_3\text{ on conversion rate of vanadium.}\]

<table>
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<tr>
<th>No.</th>
<th>MnVO4 [kg]</th>
<th>CaCO3 [kg]</th>
<th>FeV2O4 [kg]</th>
<th>CaO/V2O5</th>
<th>Vanadium conversion rate [%]</th>
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<tr>
<td>1</td>
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<td>4500</td>
<td>0.10–0.20</td>
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<td>2</td>
<td>0</td>
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<td>2500</td>
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<td>76</td>
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<td>3</td>
<td>4500</td>
<td>0</td>
<td>0</td>
<td>0.10–0.20</td>
<td>80–85</td>
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<tr>
<td>5</td>
<td>1680</td>
<td>570</td>
<td>2300</td>
<td>0.65–0.85</td>
<td>82.39</td>
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<tr>
<td>6</td>
<td>1800</td>
<td>550</td>
<td>2150</td>
<td>0.65–0.85</td>
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<td>7</td>
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<td>8</td>
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<td>435</td>
<td>1815</td>
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<td>9</td>
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<td>10</td>
<td>2585</td>
<td>270</td>
<td>1645</td>
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</table>

4.3. The Optimum Amount of MnVO4 and CaCO3

We have studied the vanadium oxidation mechanism by adding MnVO4 in calcification roasting process. The results of the effect of MnVO4 and CaCO3 on conversation rate of vanadium at M–Fe concentration 1±0.5%, rotate speed of rotary kiln 87 s/r, feed rate of mixture 4.44±0.14 kg/s, temperature of T2 for 865±10°C and temperature control curves TE, TF, TG, negative pressure of the head of rotary kiln –10±5 Pa, volume flow ratio of the air to coke oven gas 5.5 were represented in Table 8. As seen in Table 8, the amount of MnVO4 and CaCO3 has a significant effect on the conversion rate. The conversion rate was low to 76% if only there was FeV2O4, MnVO4 or CaCO3. But the conversion rate increased sharply with adjusting the amount of FeV2O4, MnVO4, CaCO3 and CaO/V2O5 ratio it passed 88% when there were 2 350 kg MnVO4, 270 kg CaCO3 and 1 750 kg FeV2O4. Therefore, the optimum amount of MnVO4 and CaCO3 was selected.
5. Conclusions

The influence of M-Fe concentration (0–6%), CaO to V₂O₅ ratio (CaO/V₂O₅ = 0.3–1.0), MnVO₄ concentration (0–57%), feed rate (1.67–5.56 kg/s), rotate speed (87–113 r/s), temperature of T2 (830–910°C), temperature control curves TA, TB, TC, TD, TE, TF, TG of connecting T1, T2, T3, T4, T5 and T6, negative pressure (−24−−6 Pa) and volume flow ratio of the combustion air to coke oven gas (5–8) were investigated. The optimum conditions for recovery 87.48–89.65% of vanadium(V) by using MnVO₄ at the M-Fe concentration 1±0.5%, CaO to V₂O₅ ratio 0.58–0.64, MnVO₄ concentration 50–55%, feed rate 4.44±0.56 kg/s, rotate speed 87–90 s/r, temperature of T2 865±10°C, temperature control curves TE, TF, TG of connecting T1, T2, T3, T4, T5 and T6, negative pressure −10±5 Pa and volume flow ratio of the air to coke oven gas (5–5.5). It was possible MnVO₄ was not only the additive but also play a key auxiliary effect for CaO with vanadium(V) to Ca₃V₂O₇ by studying on the oxidation reaction mechanism that may be represented by

\[
\text{FeV}_2\text{O}_4 + 2\text{MnVO}_4 + 3\text{CaCO}_3 + 1.25\text{O}_2 \\
= \text{Ca}_3\text{V}_2\text{O}_7 + \text{CaV}_2\text{O}_6 + \text{Mn}_2\text{O}_3 + 0.5\text{Fe}_2\text{O}_3 + 3\text{CO}_2
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REFERENCES