Industrial Application of Large Rotary Kiln for Recovery of Vanadium from Vanadium Slag Added MnVO_4 in Calcium Roasting Process

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(Received on March 3, 2017; accepted on July 14, 2017)

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 recover 87.48–89.65% of vanadium (V) by using MnVO_4 at M-Fe concentration $1 \pm 0.5\%$, CaO to V_2O_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 $865 \pm 10^\circ\text{C}$, 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 $\text{Ca}_2\text{V}_2\text{O}_7$ 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_2O_3 , V_2O_5 , FeV50, FeV80: vanadium content not less than 50% and 80% from GB4139-87) and vanadium nitride alloys in metallurgical, 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 calcifica-

tion roast-acid leaching. However, Sodium salts roast-water leaching method with one or combination of NaCl , Na_2CO_3 , and Na_2SO_4 as additive followed by water leaching has several disadvantages such as high production, leaching residue, solid waste Na_2SO_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_2O_6 , $\text{Ca}_2\text{V}_2\text{O}_7$ and $\text{Ca}_3\text{V}_2\text{O}_8$ ²¹⁾ 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_2O_5 ratio ($\text{CaO}/\text{V}_2\text{O}_5$), 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.

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-097>

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 com-

Table 1. The Chemical composition of vanadium slag studied before the removal of M·Fe.

Compound	V ₂ O ₅	TiO ₂	SiO ₂	CaO	MnO	Cr ₂ O ₃	M·Fe	T·Fe	P
mass%	20.06	11.30	14.52	2.34	9.01	1.89	18.52	27.81	0.05

Table 2. Property of vanadium slag studied after the removal of M·Fe.

Compound	T·V	CaO	M·Fe	–160 mesh	+120 mesh	–240 mesh
mass%	10.59	2.42	0.1	97.5	0.14	87.04

Table 3. Property of limestone.

Compound	CaO	–80 mesh
mass%	53.92	85.8

Fig. 1. Schematic diagram of the vanadium slag large-scale (Φ3.6×90 m) rotary kiln calcium roasting system. (Online version in color.)

pound 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 (Φ3.6×90 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 4. Experimental conditions.

Process parameters	Values
M·Fe content of fine vanadium slag [mass%]	0–6%
MnVO ₄ concentration in mixture [mass%]	0–57.5%
CaO/V ₂ O ₅ ratio in mixture [kg/kg]	0.3–1.0
Feed rate of the rotary kiln	1.67–5.56 kg/s
Rotating rate of the rotary kiln	87–113 s/r
The length of the rotary kiln	90 m
The outer diameter of the rotary kiln (Do)	3.6 m
The inner diameter of the rotary kiln (Di)	3.1 m
Gas phase	air, oxygen, coke oven gas
Solid phase	vanadium slag, limestone, MnVO ₄
Temperature of T2	830–910°C

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

60 min.

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 grinded calcification roasted clinker and leaching residue was used to detect the total amount of vanadium $[T \cdot V]$ by $NH_4S_2O_8$ oxidation and $[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$ titration method. The acid soluble $[V^{5+}]$ concentration in the calcification clinker is calculated by the mass M and $[T \cdot V]$ of clinker and residue from mass balance $([V^{5+}]_{clinker} = (M_{clinker}[T \cdot V]_{clinker} - M_{residue}[T \cdot V]_{residue})/M_{clinker})$. The conversion rate of vanadium is calculated by

$$\begin{aligned} \text{Vanadium conversion rate} &= \frac{[V^{5+}]_{clinker}}{[T \cdot V]_{clinker}} \times 100\% \\ &= \left[1 - \frac{M_{residue}[T \cdot V]_{residue}}{M_{clinker}[T \cdot V]_{clinker}} \right] \times 100\% \end{aligned} \quad \dots (1)$$

Where $[V^{5+}]_{clinker}$ and $[T \cdot V]_{clinker}$ stand for acid soluble vanadium concentration and the total vanadium concentration in clinker which roasting in rotary kiln, respectively. Reproducibility was confirmed as $\pm 2\%$ or better.

3. Experimental Results for Optimization of Process Parameters

The results of the effect of $M \cdot Fe$ concentration 0–6%, CaO/V_2O_5 ratio 0.3–1.0, $MnVO_4$ concentration 0–57.5%, feed rate 1.67–5.56 kg/s, rotate speed 87–113 s/r, temperature for T2 830–910°C, temperature control curve of connecting T1, T2, T3, T4, T5 and T6, negative pressure $-24 \sim -6$ Pa and volume flow ratio of the air to coke oven gas (5–8) on conversion rate of vanadium using calcium roasting in rotary kiln ($\Phi 3.6 \times 90$ m) are prepared as follows:

3.1. Effect of $M \cdot Fe$ Concentration in Fine Vanadium Slag

The effect of $M \cdot Fe$ 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, mass ratio of CaO to V_2O_5 in mixture 0.76 ± 0.05 , $MnVO_4$ concentration in mixture 50%, rotate speed of rotary kiln 90 s/r, temperature of T2 $870 \pm 5^\circ C$ 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. The $M \cdot Fe$ concentration in fine vanadium slag varied from 0% to 6%. The effect of $M \cdot Fe$ concentration in fine vanadium slag on conversion of vanadium was presented in Fig. 3. It was observed that the vanadium conversion rate decreased sharply from 91.14% to 53.62%. There are two reasons to explain the effect of $M \cdot Fe$ concentration in fine vanadium slag. (1) $M \cdot Fe$ which take metal iron as the principal thing act the medium during the reaction process, decreasing contact area of CaO and V_2O_5 and generating of $x \cdot CaO \cdot V_2O_5$ ($x=1,2,3$). (2) $M \cdot Fe$ change the temperature control curve of rotary kiln because of the fast exothermic reaction at the $700 \sim 1000^\circ C$, so that the content of $x \cdot CaO \cdot V_2O_5$ reduced. From this result, $1 \pm 0.5\%$ and lower concentration of $M \cdot Fe$ in fine vanadium slag was selected, which was enough to stabilize the temperature control curve

Fig. 3. Effect of $M \cdot Fe$ concentration in fine vanadium slag on vanadium conversion rate at feed rate of mixture 2.22 ± 0.14 kg/s, mass ratio of CaO to V_2O_5 in mixture 0.76 ± 0.05 , $MnVO_4$ concentration in mixture 50%, rotate speed of rotary kiln 90 s/r, temperature of T2 $870 \pm 5^\circ C$ 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.

Fig. 4. Effect of the ratio of CaO to V_2O_5 ratio in mixture on conversion rate of vanadium at $M \cdot Fe$ concentration $1 \pm 0.5\%$, feed rate of mixture 2.22 ± 0.14 kg/s, $MnVO_4$ concentration in mixture 55%, rotate speed of rotary kiln 90 s/r, temperature of T2 $870 \pm 5^\circ C$ 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.

of rotary kiln and kept high conversion rate of vanadium above 84.48%.

3.2. Effect of CaO to V_2O_5 Ratio in Mixture

The effect of CaO to V_2O_5 ratio in mixture on conversion rate of vanadium is illustrated in Fig. 4. It can be seen that the vanadium conversion rate increases with the CaO to V_2O_5 ratio, and then slightly decreases when it is above 0.64. As the CaO to V_2O_5 ratio increases further above 0.75, this effect disappears. According to the obtain result, it can be concluded that the CaO to V_2O_5 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.*²²⁾ An increase in the CaO content leads to an increase in the formation of $Ca_2V_2O_7$ due to the fact that CaO may stabilize the higher valence state of vanadium.

3.3. Effect of $MnVO_4$ Concentration in Mixture

$MnVO_4$ was the first used in the calcium roasting in

the large rotary kiln. The effect of MnVO_4 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 MnVO_4 concentration 50–55%. When MnVO_4 concentration from 50% to 57.5%, the conversion rate passed 88% and kept constant. From this result, 50–55% concentration of the MnVO_4 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 $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, MnVO_4 concentration in mixture 50–55%, rotate speed of rotary kiln 87–90 s/r, temperature T2 of $870 \pm 5^\circ\text{C}$ 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 rare 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 conversion rate at M·Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, MnVO_4 concentration in mixture 50–55%, feed rate of mixture 4.44 ± 0.14 kg/s, temperature T2 of $870 \pm 5^\circ\text{C}$ 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.

Fig. 5. Effect of MnVO_4 concentration in mixture on conversion rate of vanadium at M·Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, feed rate of mixture 2.22 ± 0.14 kg/s, rotate speed of rotary kiln 90 s/r, temperature of T2 $870 \pm 5^\circ\text{C}$ 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.

3.6. 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 $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, MnVO_4 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, $865 \pm 10^\circ\text{C}$ 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 $865 \pm 10^\circ\text{C}$ and temperature control curves TE, TF, TG are selected.

Fig. 6. Effect of feed rate of mixture on conversion rate of vanadium at M·Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, MnVO_4 concentration in mixture 50–55%, rotate speed of rotary kiln 90 s/r, temperature of T2 $870 \pm 5^\circ\text{C}$ 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.

Table 5. The conversion rate of vanadium at different rotating rate of the rotary kiln.

Rotating rate [s/r]	Vanadium conversion rate [%]
82	91.45
87	89.65
90	87.48
113	84.49

Fig. 7. Effect of reaction temperature on conversion rate of vanadium at M-Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, $MnVO_4$ 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.

Table 6. The conversion rate of vanadium at different temperature distribution of the rotary kiln.

T [°C]	L [m]	TA	TB	TC	TD	TE	TF	TG
T1	3	666	646	687	674	672	658	679
T2	13	839	855	855	858	857	865	854
T3	23	822	800	801	805	805	842	831
T4	33	803	772	777	780	778	810	806
T5	48	768	734	712	716	692	629	674
T6	73	491	580	516	502	483	337	372
Vanadium conversion rate [%]		85.74	88.88	88.1	87.18	90.3	91.38	91.35

Fig. 8. Effect of negative pressure on conversion rate of vanadium at M-Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, $MnVO_4$ concentration in mixture 50–55%, feed rate of mixture 4.44 ± 0.14 kg/s, rotate speed of rotary kiln 87 s/r, temperature of T2 $870 \pm 5^\circ\text{C}$ at the length of rotary kiln 13 m, volume flow ratio of the air to coke oven gas 5.5.

3.7. Effect of Negative Pressure on Conversion Rate of Vanadium

Figure 8 illustrates the conversion rate of vanadium, as a function of negative pressure studied. As shown in this

Fig. 9. Effect of volume flow ratio of the air to coke oven gas on conversion rate of vanadium at M-Fe concentration $1 \pm 0.5\%$, CaO to V_2O_5 ratio of 0.58–0.64, $MnVO_4$ concentration in mixture 50–55%, feed rate of mixture 4.44 ± 0.14 kg/s, rotate speed of rotary kiln 87 s/r, temperature of T2 $865 \pm 10^\circ\text{C}$, negative pressure of the head of rotary kiln -10 ± 5 Pa.

figure, 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 ± 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. It can be seen the vanadium conversion rate decreased with decreasing the volume flow ratio of the air to coke oven gas. Therefore, 5–5.5 of volume flow ratio of the air to coke oven gas is selected.

4. Discussion

4.1. Optimum Temperature Condition for Recover of Vanadium

Temperature conditions including master temperature point of T2 and optimal temperature control curves of connecting T1, T2, T3, T4, T5 and T6 are selected in section 3.6 as shown in Fig. 7 and Table 6. Master temperature point of T2 which is closest to the flame and can represent the highest temperature in the kiln is higher than 900°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 T2 is low than 850°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 T2 is not enough, temperature control curves of connecting T1, T2, T3, T4, T5 and T6 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 T3, T4, T5 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 control 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 also had to continue with the increase of calcination temperature of gas, so repeat the exception production vicious circle of “T3, T4 high temperature control—cooling heating temperature control—T3, T4 high temperature control”. At the same time, the temperature control of high above 900°C lead to clinker melt into liquid phase, cooling treatment into the relatively low temperature zone lead to liquid phase condensation of solid phase that bonding in the kiln wall. A part of the powder bonding package into the ball of the rotary kiln and rotating roll “snow ball” the way to grow up, the maximum reached more than 1.2 m, and the internal and external vanadium conversion rates were 9% and 55%, respectively. Roasting clinker’s hardness was very big that difficult to break, it seriously affected the normal operation of the rotary kiln and the yield of vanadium. Therefore, Second production stage after December 2013, it is needed to discuss about the influence of the above operation factors

in industrial application of large rotary kiln for recovery of vanadium from vanadium slag added MnVO_4 in calcium roasting process on the temperature stability in below Section 4.2.

4.2. The Influence of the Above Operation Factors on the Temperature Stability

The influence of the above operation factors such as M·Fe concentration, $\text{CaO}/\text{V}_2\text{O}_5$ ratio, MnVO_4 concentration, feed rate, rotate speed, negative pressure and the volume of combustion air, coke oven gas, oxygen as shown in Section 3 on 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 $\text{Fe} + [\text{O}] = \text{FeO}$, $2\text{Fe} + 3[\text{O}] = \text{Fe}_2\text{O}_3$, $3\text{Fe} + 4[\text{O}] = \text{Fe}_3\text{O}_4$. It is typical of magnetochemical 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) $\text{CaO}/\text{V}_2\text{O}_5$ 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_2O_4) in the inner was oxidized to V_2O_5 at 210–660°C and reacted with calcium oxide decomposed by CaCO_3 at 550–700°C. Calcium vanadate $\text{Ca}(\text{VO}_3)_2$, $\text{Ca}_2\text{V}_2\text{O}_7$, $\text{Ca}_3(\text{VO}_4)_2$ were produced at different theoretical $\text{CaO}/\text{V}_2\text{O}_5$ ratio of 0.31, 0.63, 0.92 and different roasting temperature at 600–880°C as shown in below:²³⁾

Major vanadate $\text{Ca}_2\text{V}_2\text{O}_7$ can be easy to leach with sulfuric acid because of theoretical $\text{CaO}/\text{V}_2\text{O}_5$ ratio of 0.45–0.63 while $\text{Ca}(\text{VO}_3)_2$, $\text{Ca}_3(\text{VO}_4)_2$ was hard to leach due to its low content and poor crystallinity.²³⁾ The lower the $\text{CaO}/\text{V}_2\text{O}_5$ ratio of low limestone and more vanadium slag, the higher the roasting temperature for feeding temperature between T6 and T5. The higher the $\text{CaO}/\text{V}_2\text{O}_5$ ratio of more

Fig. 10. Effect of temperature curves on vanadium conversion rate.

Table 7. The effect of different operating parameters on conversation rate of vanadium for 4.44 kg/s feed rate.

No.	rate [%]	T1 [°C]	T2 [°C]	T3 [°C]	T4 [°C]	T5 [°C]	T6 [°C]	P [Pa]	Air [Nm ³ /s]	Gas [Nm ³ /s]	O ₂ [vol%]
1	14.97	400	757	684	626	540	445	−5	1.43	0.25	21.8
2	67.82	604	836	704	590	417	200	−7	1.87	0.31	19.5
3	84.57	603	861	831	802	627	372	−10	1.64	0.32	15.9
4	92.12	646	863	830	803	634	459	−2	1.59	0.30	13.34

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.^{24,25)}

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 factor which leads to the runaway of rotary kiln temperature. The most effective way is to add a kind of inert material to absorb the oxidation reaction heat to further stabilize the whole kiln temperature control. So inert material MnVO₄ was added dilution reaction heat in calcium roasting process.

(4) Feed rate mainly affects the feed temperature curve stability between inlet and T5 temperature. The feed temperature curve moved up and down with the feed rate increase and decrease. If the feed rate is fluctuations, temperature stability greatly affected.

(5) Rotate speed mainly affects roasting time. With the increase of the roasting time, the possibility of the formation of the ring increases, the condition in the kiln becomes worse, and the temperature stability becomes worse.

(6) The negative pressure affects the temperature stability, mainly the temperature stability of the middle and rear section, which is affected by the temperature and velocity of the gas. With the increase of the negative pressure, the temperature of the kiln is improved and stable, but the temperature velocity is too fast, resulting in the reaction is not sufficient and the vanadium conversion rate is low.

(7) Combustion air, coke oven gas, oxygen flow is also one of the important factors that affect the temperature stability. The temperature curve change with combustion air, coke oven gas, oxygen flow. The coke oven gas flow rate directly affects the level of T2, T3, T4 temperature, the combustion air flow rate directly affects the level of auxiliary control temperature T5, T6 and the oxygen flow mainly affects the full extent of the gas combustion supply temperature.

Operation factors M·Fe concentration, CaO/V₂O₅ ratio, 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.

4.3. 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 $1 \pm 0.5\%$, rotate speed of rotary kiln 87 s/r, feed rate of mixture 4.44 ± 0.14 kg/s, temperature of T2 for $865 \pm 10^\circ\text{C}$ 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 conversation rate was low to 76% if only there was FeV₂O₄, MnVO₄ or CaCO₃. But the conversation 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.

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

According to the above experiment data, discussion and reference,^{23–25)} 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 ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$, $\text{V}^{3+} \rightarrow \text{V}^{4+} \leftarrow \text{V}^{5+}$), produce MnO and V₂O₄ sharply is oxidized and recombine into MnVO₄.

Table 8. The effect of MnVO₄ and CaCO₃ on conversation rate of vanadium.

No.	MnVO ₄ [kg]	CaCO ₃ [kg]	FeV ₂ O ₄ [kg]	CaO/V ₂ O ₅	Vanadium conversation rate [%]
1	0	0	4 500	0.10–0.20	≤20
2	0	600	2 500	0.65–0.85	76
3	4 500	0	0	0.10–0.20	80–85
5	1 680	570	2 300	0.65–0.85	82.39
6	1 800	550	2 150	0.65–0.85	84.95
7	2 000	470	2 030	0.65–0.85	87.4
8	2 250	435	1 815	0.65–0.85	89.95
9	2 350	270	1 750	0.45–0.65	91.42
10	2 585	270	1 645	0.45–0.65	88.86

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

(2) Oxidation reaction stage from T6 to T5: CaCO_3 is decomposed into CaO and CO_2 from 550°C to 700°C ²⁶⁾ ($\text{CaCO}_3 = \text{CaO} + \text{CO}_2$). Low melting point material of V_2O_3 , V_2O_4 , V_2O_5 and Fe_2O_3 form the solid pellet $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_3$, $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_4$, $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$ ²⁶⁾ and continue oxidation as describe by

(3) Oxidative calcification stage from T5 to T2: solid pellet $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_3$, $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_4$, $\text{Fe}_2\text{O}_3 \cdot \text{V}_2\text{O}_5$ decomposes into V_2O_3 , V_2O_4 , V_2O_5 and Fe_2O_3 . V_2O_5 reacts initially with CaO to form calcium vanadate $\text{Ca}(\text{VO}_3)_2$, $\text{Ca}_2\text{V}_2\text{O}_7$, $\text{Ca}_3(\text{VO}_4)_2$ at different theoretical $\text{CaO}/\text{V}_2\text{O}_5$ ratio of 0.31, 0.63, 0.92 and different roasting temperature as shown in Eqs. (3)–(5) in Section 4.2.

According to above equation, from feed stage to cooling stage between inlet and outlet, the calcification roasting chemistry reaction mechanism of vanadium may be represented by

5. Conclusions

The influence of $\text{M}\cdot\text{Fe}$ concentration (0–6%), CaO to V_2O_5 ratio ($\text{CaO}/\text{V}_2\text{O}_5$)(0.3–1.0), MnVO_4 concentration (0–57.5%), feed rate (1.67–5.56 kg/s), rotate speed (87–113 r/s), temperature of T2 ($830\text{--}910^\circ\text{C}$), temperature control curves TA, TB, TC, TD, TE, TF, TG of connecting T1, T2, T3, T4, T5 and T6, negative pressure ($-24\text{--}-6$ Pa) and volume flow ratio of the combustion air to coke oven gas (5–8) were investigated. The optimum conditions for recover 87.48–89.65% of vanadium(V) by using MnVO_4 at the $\text{M}\cdot\text{Fe}$ concentration $1\pm 0.5\%$, CaO to V_2O_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 $865\pm 10^\circ\text{C}$, 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 MnVO_4 was not only the additive but also play a key auxiliary effect for CaO with vanadium(V) to $\text{Ca}_2\text{V}_2\text{O}_7$ by studying on the oxidation reaction mechanism that may be represented by

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