

Extraction of vanadium from molten vanadium bearing slag by oxidation with pure oxygen in the presence of CaO

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Abstract: A novel process of vanadium extraction from vanadium slag in its molten state was conducted at the laboratory scale by oxidation with pure oxygen in the presence of CaO. The effect of mass ratio of CaO to V_2O_5 on the recovery of vanadium was studied. The sintered samples were leached by H_2SO_4 solution and characterized by XRD, XPS, SEM and EDS techniques. Compared with the roasting process, the energy saving effect of the proposed process was also discussed. The results showed that vanadium-rich phases were formed and vanadium mainly existed in the forms of CaV_2O_5 and $Ca_2V_2O_7$. The formation mechanism of calcium vanadates in the molten vanadium bearing slag was explained. The XRD and XPS results implied that there was a limit to the oxidation reaction of V(IV) to V(V) under the high temperatures even though oxygen-supply was sufficient. An increase in the CaO content led to an increase in the formation of $Ca_2V_2O_7$. About 90% of the vanadium recovery was obtained under optimal experiment conditions (mass ratio of CaO to V_2O_5 of 0.6, particle size 120 μm , leaching temperature 90 °C, leaching time 2 h, H_2SO_4 concentration 20%, liquid to solid ratio 5:1 mL/g, stirring speed 500 r/min). The energy of 1.85×10^6 kJ could be saved in every 1000 kg of vanadium bearing slag using the proposed process from the theoretical calculation results. Recovery of vanadium from the molten vanadium bearing slag and utilisation of its heat energy are important not only for saving metal resources, but also for energy saving and emission reduction.

Key words: molten vanadium bearing slag; CaO; oxidation; acid leaching; vanadium recovery; energy saving effect

1 Introduction

Vanadium is an important product that is used almost exclusively in ferrous and non-ferrous alloys due to its physical properties such as high tensile strength, hardness, and fatigue resistance [1–4]. Vanadium–titanium magnetite ore is one of the main ore feedstocks for the recovery of vanadium in China and significant quantities of vanadium bearing slag (V-slag) containing 12%–20% V_2O_5 is generated as byproduct from the iron or steel industries [5,6]. The recovery methods of vanadium from V-slag have recently been discussed. A well-known process of roasting–leaching operation was introduced to recover vanadium from V-slag. Firstly, the slag is roasted in a multiple hearth furnace or a rotary

kiln under alkaline conditions. The salt-roasting process involves first the preparation of mixtures of sized ore with a sodium salt which can be one or combination of NaCl, Na_2CO_3 and Na_2SO_4 under an oxidizing atmosphere, which will convert the vanadium values of V-slag into water-soluble sodium vanadate [7–9]. In some cases, lime is also used in the roasting stage [10,11], and calcium vanadate formed in roasting can be dissolved by leaching with acid or alkali. After roasting, the vanadium is transferred to the aqueous phase through hydro-leaching and is precipitated from the solution upon adding ammonia and controlling the pH via sulphuric acid. After removal of the ammonia, the vanadate can be converted to various oxide forms such as V_2O_3 and V_2O_5 [12–14].

However, there is a large amount of heat waste in

this roasting–leaching process. Molten V-slag after natural cooling needs to be reheated again, that is, its physical heat has been wasted. For an enterprise with an annual output of 300 kt V-slag, ca. 3.688×10^{13} kJ of heat energy will be wasted for roasting. In order to use this heat, a new concept of extracting vanadium from molten vanadium slag was proposed by University of Science and Technology Beijing [15,16]. Based on this concept, the aim of this work is to research a novel technology of extracting vanadium from molten V-slag by means of oxidation with pure oxygen in the presence of lime characterized by more efficient and energy saving.

The previous work was focused on the vanadium extraction from molten V-slag using sodium carbonate (Na_2CO_3) as an additive [17]. However, due to the limitations of thermodynamic conditions, the oxidizing reaction of V(IV) to V(V) is incomplete at a higher temperature in molten V-slag system, which will lead to the loss of vanadium because only V(V) compounds are water-soluble [18]. To cope with this limitation, a novel technology using CaO instead of Na_2CO_3 as the additive followed with acid leaching was conducted at the laboratory scale. The current work focused on the study of vanadium extraction from molten vanadium using this method and the energy saving effect of this work will be discussed.

2 Experimental

2.1 Materials and methods

The V-slag used in this study was obtained from Kapok Iron and Steel Corporation, Sichuan Province, China. The original slag samples were crushed and ground to 120 to 150 μm . Its semi-quantitative composition was analyzed by X-ray fluorescence (XRF–1800, Shimadzu, Japan) and the results are given in Table 1. All the reagents used were of analytical reagent grade, and were dried at 393 K for 6 h before using. The mineralogical composition of the samples was identified by a powder X-ray diffraction system (XRD, Rigaku TTR-III, Japan) equipped with Cu K_α radiation. The surface morphology and element composition of the sintered samples were examined by a scanning electron microscope (SEM, JSM–6480 LV, Japan) equipped with an energy dispersive spectroscopy (EDS, Noran System six, American). The valence state of vanadium in sample surface was studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis-Ultra DLD, Japan). XPS data reduction of the measured high-resolution spectral envelopes was thence performed by curve fitting synthetic peak components using the software CasaXPS (Casa Software Ltd., UK). The calibration was achieved using the C1s peak of the surface contamination at 284.6

eV. The relative amount of the V(V), V(IV) and V(III) on the sample surface was obtained from integration of the V 2p core level spectra.

Table 1 Chemical composition of vanadium slag (mass fraction, %)

FeO	SiO ₂	V ₂ O ₃	TiO ₂	MnO
32.3	21.1	14.2	12.0	8.7
MgO	Al ₂ O ₃	CaO	P ₂ O ₅	
4.6	4.2	2.6	0.2	

2.2 Melting oxidation experiment

The experimental temperature was 1450 °C to keep the V-slag in molten state. Pure oxygen was used to produce an oxidizing atmosphere. A heating furnace with heating element of silica carbide tube was employed in the melting process. The temperature of the furnace was controlled electronically within ± 5 °C via a thermocouple placed closed to the bottom of the protective crucible. The schematic diagram of the whole experimental apparatus is shown in Fig. 1. In all the experiments, an Al₂O₃ crucible containing 80 g V-slag was placed in the furnace and heated to 1450 °C at the rate of 10 °C/min in a protective atmosphere. Holding 1450 °C for 5 min made the V-slag melt fully. Then we cut off the power and charged CaO into the molten V-slag through a quartz tube. The pure oxygen was then blown into the slag immediately by a double-hole alumina tube ($d=1$ mm of each hole), which can help the process of oxidation reaction. Different mass ratios of CaO to V₂O₅ ranging from 0.15 to 1.0 by changing the amount of CaO were considered and sufficient oxygen was used in this experiment. After the melting process was completed, the sinters were taken out and cooled with water quenching, then crushed and ground to 120 to 150 μm for further analysis. The mineral compositions, surface morphology and element composition of the sintered samples were determined by XRD, XPS, SEM and EDS using the above-mentioned conditions.

2.3 Acid leaching

The leaching experiments were performed at an atmospheric pressure in a magnetic stirrer capable of heating and stirring. In all the leaching experiments, 5 g of the sintered samples was leached in a 15% sulfuric acid solution at 90 °C for 2 h. The ratio of liquid to solid (L/S ratio) was 5:1 (mL/g), and the stirring speed was 500 r/min. To determine the effect of sulfuric acid (H_2SO_4) concentration, the H_2SO_4 concentration range applied was 5% to 30% at an interval of 5%. These optimum parameters were chosen according to the present research results [19–23]. After each leaching test, the leach slurry was separated via vacuum filtration, and

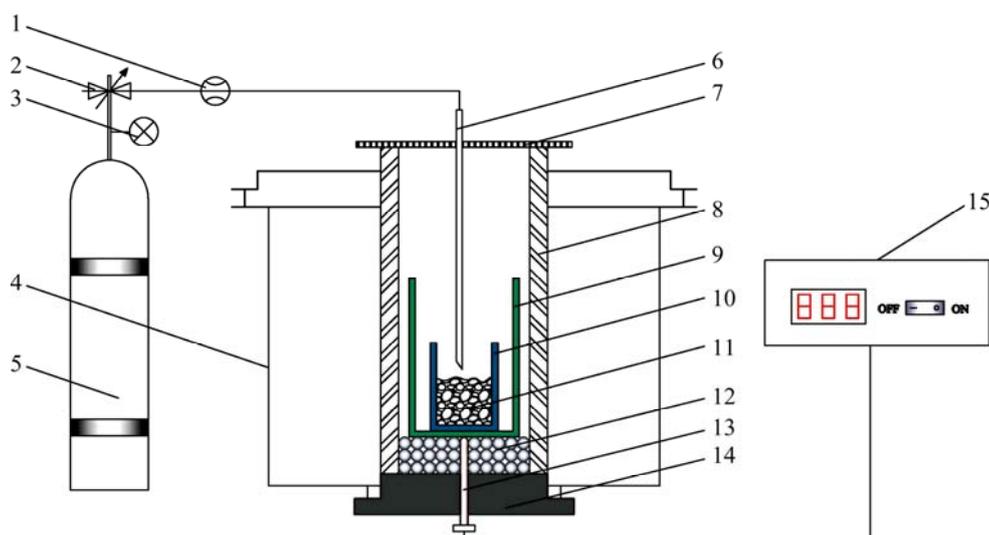


Fig. 1 Schematic diagram of experimental apparatus: 1—Floater flowmeter; 2—Valve; 3—Pressure gauge; 4—Furnace shell; 5—Oxygen cylinder; 6—O₂ inlet tube; 7—Furnace lid; 8—Thread silica carbide tube; 9—Al₂O₃ protective crucible; 10—Al₂O₃ crucible; 11—Molten V-slag; 12—Corundum spheres; 13—Thermocouple; 14—Pedestal; 15—Temperature control instrument

the residue was washed with deionized water. The total vanadium contents in the sintered samples and filtrates were determined by ferrous ammonium sulfate titration method to determine the amount of vanadium pentoxide in the leaching solution [24,25].

3 Results and discussion

3.1 Mineralogical analysis

As shown in Fig. 2, it is revealed that the major phases in original V-slag are vanadium-bearing spinel, olivine, and cristobalite. Vanadium existing as V(III) is mostly located in the spinel phase with large particle sizes.

Figure 3 presents the XRD patterns of the sintered samples at different CaO to V₂O₅ ratios. The XRD results in Fig. 3 reveal that the major vanadium bearing phases in the sintered samples are CaV₂O₅ and Ca₂V₂O₇. The diffraction peaks of CaV₂O₅ increase with CaO to V₂O₅ ratio, and then decrease when this ratio is above 0.60. Meanwhile, the diffraction peaks of Ca₂V₂O₇ appear, and the spectrum intensity of Ca₂V₂O₇ increases obviously with the increase of CaO to V₂O₅ ratio, indicating that CaO may stabilize the higher valence states of vanadium. The existence of CaV₂O₅ implies an incomplete oxidation of vanadium, and it also means that there is a limit to the oxidation reaction of V(IV) to V(V) in the melting experiment at a higher temperature. As shown in equation (1), the free energy change is close to zero at temperature above 1673 K (1400 °C) in the standard state. Therefore, the oxidation reaction of V(IV) to V(V) in the molten V-slag is not thermodynamically beneficial.

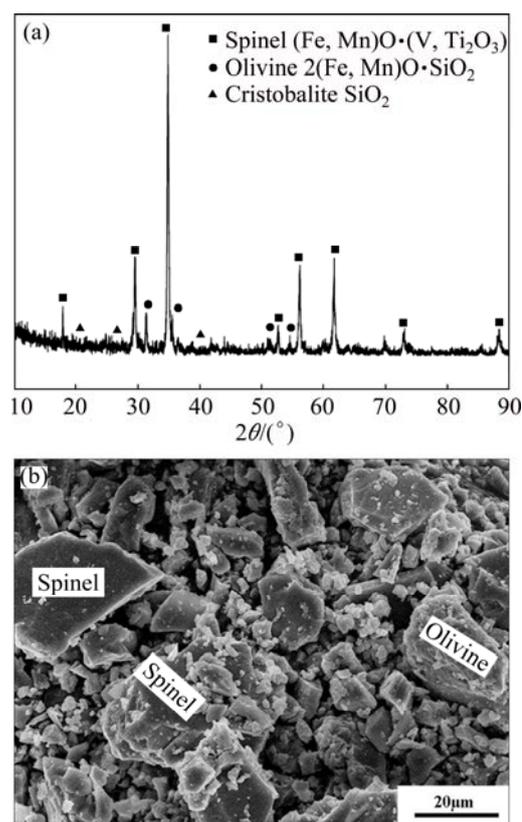
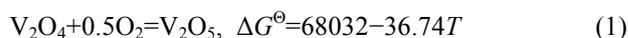


Fig. 2 XRD pattern (a) and SEM image (b) of original V-slag sample



XPS study results of the vanadium valence state in the sintered sample surfaces are shown in Fig. 4 and Table 2. XPS data used in the peak separations were obtained from previous researches [26,27]. The binding energies of V(IV) 2p_{3/2} and V(V) 2p_{3/2} are measured as

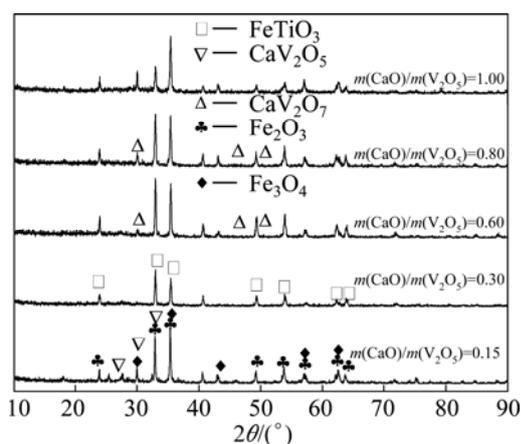


Fig. 3 XRD patterns of sintered samples at different mass ratios of CaO to V_2O_5

516.4 eV and 517.3 eV, respectively. It can be seen that the sintered samples are not fully oxidized. Vanadium exists as V(IV) and V(V). By increasing the content of CaO, relative proportion of V(V)/V(V)+V(IV) obtained from curve fit will be enhanced, which is found to agree with the XRD results. The highest relative proportion of V(V)/V(V)+V(IV) in this work is 66.55%.

Based on the results, the formation mechanism of

Table 2 Result of XPS analyses for V $2p_{3/2}$ in sintered samples shown in Fig. 4

Fig. 4	V $2p_{3/2}$	Binding energy/eV	Relative proportion/%	FWHM/eV
(a)	V(V)	517.3	56.58	1.33
	V(IV)	516.4	43.42	1.48
(b)	V(V)	517.3	61.92	1.35
	V(IV)	516.4	38.08	1.52
(c)	V(V)	517.3	63.82	1.35
	V(IV)	516.4	36.18	1.50
(d)	V(V)	517.3	66.55	1.36
	V(IV)	516.4	33.45	1.56

calcium vanadates in the molten V-slag can be explained in detail as follows: V_2O_5 is oxidized by the pure oxygen and the main oxidation products are V_2O_4 and V_2O_5 ; when CaO is added, CaO intensely combines with V_2O_4 and V_2O_5 to yield CaV_2O_5 and $Ca_2V_2O_7$, respectively. 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 states of vanadium.

Figure 5 shows the SEM images of the sintered samples at different CaO to V_2O_5 ratios and the corresponding EDS analysis is listed in Table 3. The

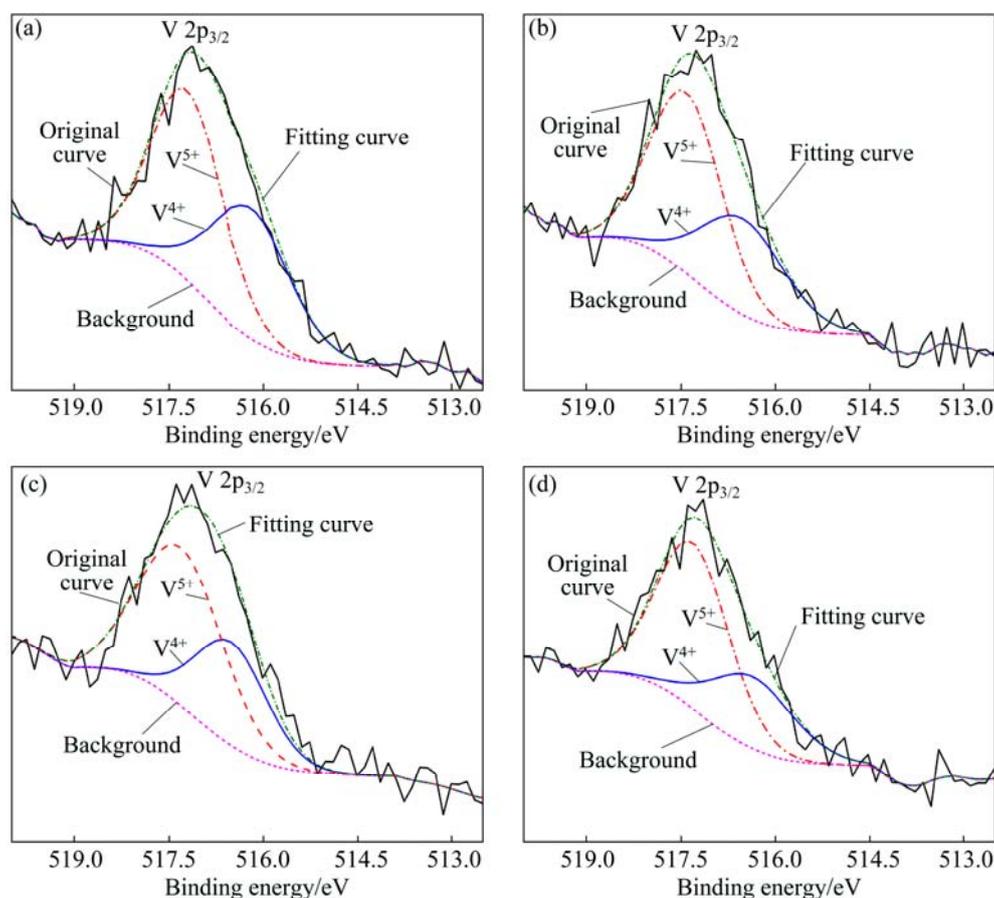


Fig. 4 Vanadium 2p photoemission spectra for sintered samples at different mass ratios of CaO to V_2O_5 : (a) 0.15; (b) 0.30; (c) 0.60 (d) 1.00

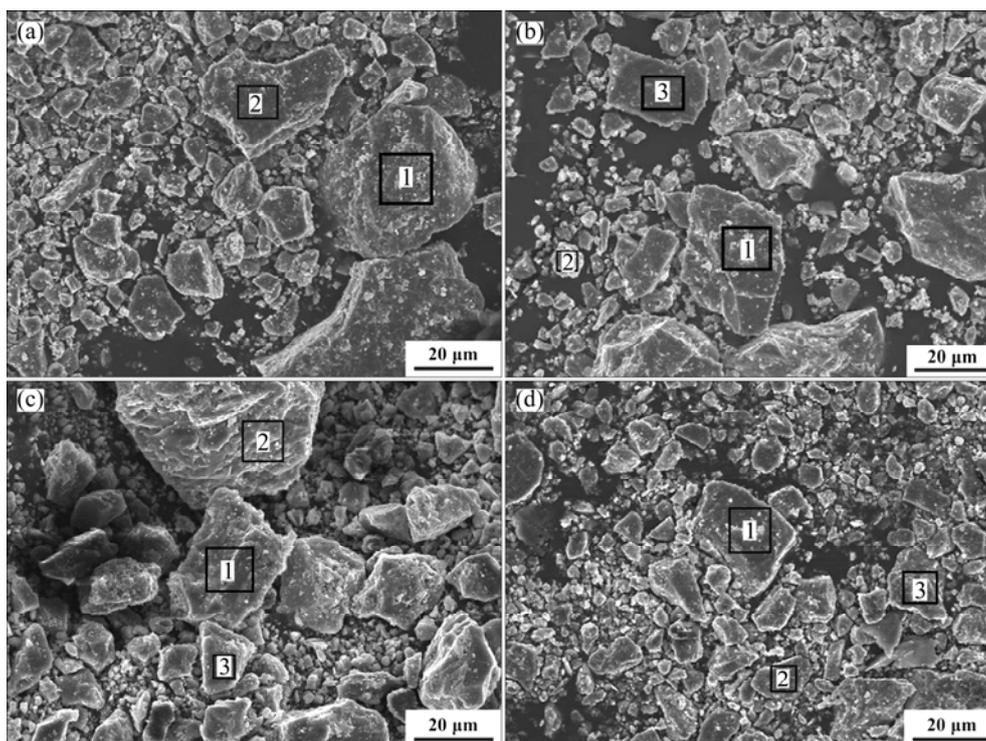


Fig. 5 SEM images of sintered samples at different mass ratios of CaO to V_2O_5 : (a) 0.15; (b) 0.30; (c) 0.60; (d) 1.00

Table 3 EDS analysis of sintered samples at different mass ratios of CaO to V_2O_5 ratios (mass fraction, %)

Region in Fig. 5	O	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe
(a)-1	28.18	1.44	4.39	9.61	2.86	7.08	13.75	0.32	8.29	23.67
(a)-2	30.85	1.90	4.68	9.17	0.50	3.90	7.67	0.58	5.82	34.94
(b)-1	40.58	1.59	6.57	12.51	4.37	4.12	10.35	0.14	6.30	13.46
(b)-2	49.69	3.35	3.00	15.89	1.45	1.52	2.69	0.21	4.73	17.46
(b)-3	17.75	0.40	2.86	1.68	3.53	8.75	12.40	0.78	8.09	43.76
(c)-1	14.13	0.82	5.35	6.01	10.64	9.32	15.53	–	7.23	30.98
(c)-2	34.49	1.52	5.20	9.76	9.03	4.17	12.08	1.60	6.84	15.30
(c)-3	38.21	4.19	2.82	2.51	1.53	0.78	2.75	0.32	10.33	36.56
(d)-1	27.67	0.53	3.61	8.40	13.95	7.81	15.24	0.20	5.20	17.40
(d)-2	23.26	1.02	3.61	3.09	2.69	10.27	4.61	0.26	4.73	46.47
(d)-3	41.95	1.01	5.99	13.23	13.31	2.57	13.32	–	5.10	3.52

sinter particles in Fig. 5 present an irregular shape. Also, it is observed that V, Ca, Mn and Si are concentrated in the dark gray region, and Fe and O distribute in the whole region; Ti, Al, Mg and Cr are irregularly distributed in the sintered samples. As shown in the SEM/EDS results, the Ca–V-rich phases were gradually formed with the increasing mass ratio of CaO to V_2O_5 . When CaO content in the V-slag is small, vanadium oxide will react with iron oxide or manganese oxide to yield iron vanadate or manganese vanadate besides CaO. As the content of CaO increases, vanadium oxide will intensely interact with CaO to form more Ca–V-rich phases. It is worth mentioning that the high Al content

shown in Fig. 5 may be from the alumina tube used in the melting oxidation experiment.

3.2 Sulfuric acid leaching results

3.2.1 Effect of $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio

The sintered samples at different $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratios were leached in sulfuric acid solutions. The H_2SO_4 concentration was 15% at liquid to solid ratio of 5:1 mL/g. Other leaching parameters were mentioned above. The effect of $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio on the vanadium recovery is illustrated in Fig. 6. It can be seen that the vanadium recovery increases with the $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio, and then slightly decreases when it is above 0.8.

This behavior may be due to experimental error. As the $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio increases further, this effect disappears, and these data are not shown in diagram. According to the obtained results, it can be concluded that the $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio of 0.6 is the best result, which is supported by XRD. With this ratio, vanadium recovery will be enhanced up to 88%.

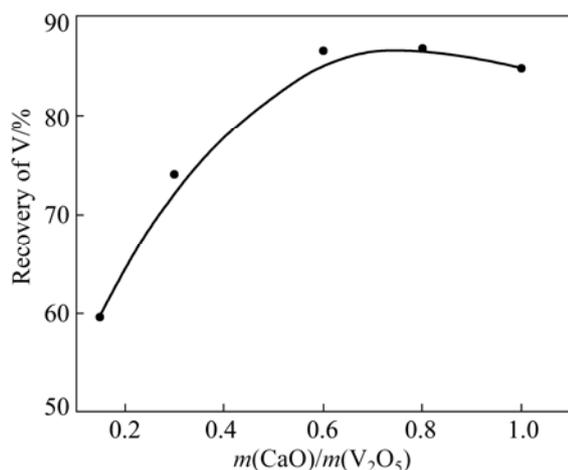


Fig. 6 Effect of $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio on vanadium recovery (H_2SO_4 concentration: 15%; L/S ratio: 5:1 mL/g; leaching temperature: 90 °C; leaching time: 2 h; stirring speed: 500 r/min; particle size: 120–150 μm)

3.2.2 Effect of sulfuric acid concentration

Experiments were carried out by varying the concentration of H_2SO_4 from 5% to 30%. Figure 7 illustrates the recovery curve of vanadium as a function of H_2SO_4 concentration. As seen, the recovery of vanadium increases at elevated H_2SO_4 concentration up to 20% and leveled out at higher H_2SO_4 concentrations. Approximately, 90% recovery of vanadium was obtained

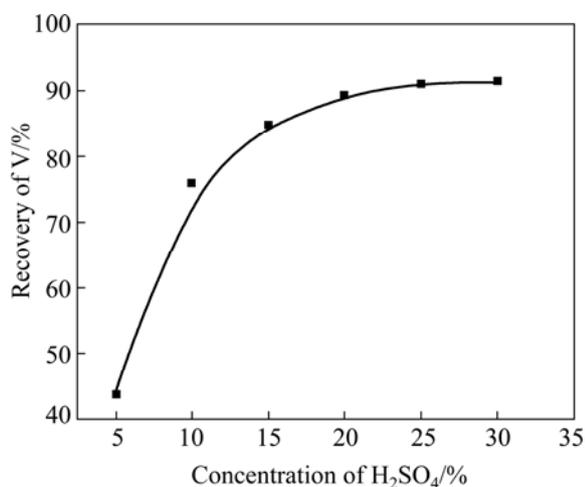


Fig. 7 Effect of concentration of H_2SO_4 on recovery of vanadium ($m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio: 0.6; L/S ratio: 5:1 mL/g; leaching temperature: 90 °C; leaching time: 2 h; stirring speed: 500 r/min; particle size: 120–150 μm)

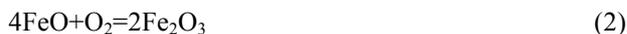
by using 20% H_2SO_4 concentration. There would be more impurities and limited contribution to improvement of vanadium recovery following the further increase of the H_2SO_4 concentration.

Based on the results, we assume that the optimum conditions of $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ ratio and H_2SO_4 concentration for vanadium recovery are 0.6 and 20%, respectively.

3.3 Energy saving calculation

The main benefit for this novel technology is to reduce the roasting energy. However, pure oxygen, as an energy carrier, will be used in the new system compared with the old system, which brings extra energy consumption. Therefore, the energy saving effect of our proposed process still needs to be verified by a detailed calculation. The assumed conditions in our calculations are shown as follows: 1000 kg of V-slag and 96 kg of CaO, according to the $m(\text{CaO})/m(\text{V}_2\text{O}_5)$ of 0.6, were chosen in the vanadium extraction process; a theoretical value of oxygen demand will be calculated according to the composition of V-slag shown in Table 1 to make sure that all the oxides are in their high valence state; the roasting temperature is 900 °C (1173 K); the energy consumption of oxygen production is about 2.16×10^6 kJ/m³ [28]; heat recovery of roasting process is not considered.

In order to simplify the calculation, the energy consumption of the proposed process E_O is measured by the oxygen consumption of equations (2) and (3), and meanwhile, that of roasting process is estimated by the endothermic quantity of heating V-slag and CaO from 298 K to 1173 K without considering the energy consumption of mixing and pelletizing. The energy conversion efficiency (φ) is introduced for the heat loss of roasting equipment such as exhaust fume heat, radiant heat and natural convective heat in roasting process. Then the energy consumption of the roasting process (E_r) can be described by equation (4).



$$E_r = \frac{1}{\varphi} (m_{\text{slag}} \int_{298}^{1173} c_{p,\text{slag}} dT + m_{\text{CaO}} \int_{298}^{1173} c_{p,\text{CaO}} dT) \quad (4)$$

where φ is the energy conversion efficiency; m and c are the mass and the specific heat capacity, respectively; T is the temperature. Values of these parameters and the calculation results are shown in Table 4. It can be seen that the E_O is far less than E_r , and the energy of 1.85×10^6 kJ ($E_r - E_O$) will be saved by using the proposed process compared with the roasting process when 1000 kg of V-slugs is used for extracting vanadium.

Table 4 Parameters and results for calculations

Parameter	$m_{\text{slag}}/\text{kg}$	m_{CaO}/kg	$\varphi/\%$	$c_{p,\text{slag}}/(\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1})$	$c_{p,\text{CaO}}/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$	E_0/kJ	E_r/kJ
Value	1000	96	60	1.248	$49.62+4.52\times 10^{-3}T^2-6.95\times 10^5T^{-2}$	9.68×10^4	1.95×10^6
Source	Set value	Calculation	Estimate	Ref.[29]	Ref. [30]	Calculation	Calculation

4 Conclusions

1) A direct oxidation and acid leaching process, using CaO and sulfuric acid as the additive and leaching agent respectively, was carried out to extract vanadium from molten vanadium bearing slag to make use of its heat energy. Compared with the roasting process, the energy saving effect calculation of the proposed process was also performed.

2) By means of oxidation with pure oxygen and adding CaO, vanadium in molten vanadium bearing slag is oxidized and the main oxidation products are V_2O_4 and V_2O_5 . When CaO is added, CaO intensely combines with V_2O_4 and V_2O_5 to yield CaV_2O_5 and $\text{Ca}_2\text{V}_2\text{O}_7$, respectively. The XRD and XPS results imply that there is a limit to the oxidation reaction of V(IV) to V(V) under the high temperatures even though oxygen-supply is sufficient. An increase in the CaO content leads to an increase in the formation of $\text{Ca}_2\text{V}_2\text{O}_7$. It is found that the Ca–V-rich phases are formed in the sintered samples from the SEM/EDS results.

3) About 90% of the vanadium recovery was obtained under optimal experiment conditions (mass ratio of CaO to V_2O_5 of 0.6, particle size 120 to 150 μm , leaching temperature 90 $^\circ\text{C}$, leaching time 2 h, liquid to solid ratio 5:1 mL/g, stirring speed 500 r/min). The energy of 1.85×10^6 kJ will be saved in every 1000 kg of V-slag using the proposed process from the theoretical calculation results. It is proved from the experimental and calculating results that it is an effective method for the recovery of vanadium from vanadium bearing slag in its molten state.

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References

- [1] MOSKALYK R R, ALFANTAZI A M. Processing of vanadium: A review [J]. *Minerals Engineering*, 2003, 16: 793–805.
- [2] TAYLOR P R, SHUEY S A, VIDAL E E, GOMEZ J C. Extractive metallurgy of vanadium containing titaniferous magnetite ores: A review [J]. *Minerals & Metallurgical Processing*, 2006, 23: 80–86.
- [3] LAN Y Z, LIU J. Review of vanadium processing in China [J]. *Engineering Sciences*, 2005, 3: 58–62.
- [4] WANG M Y, XIAO L S, LI Q G, WANG X W, XIANG X Y. Leaching of vanadium from stone coal with sulfuric acid [J]. *Rare Metals*, 2009, 28: 1–4.
- [5] ZHANG Y M, BAO S X, LIU T, CHEN T J, HUANG J. The technology of extracting vanadium from stone coal in China: History, current status and future prospects [J]. *Hydrometallurgy*, 2011, 109: 116–124.
- [6] GUSTAFSSON S, WANG W. Recovery of vanadium from hot metal [J]. *International of Mineral Processing*, 1985, 15: 103–115.
- [7] SADYKHOV G B. Oxidation of titanium–vanadium slags with the participation of Na_2O and its effect on the behavior of vanadium [J]. *Russian Metallurgy (Metally)*, 2008, 2008(6): 449–458.
- [8] LI X S, XIE B, WANG G E, LI X J. Oxidation process of low-grade vanadium slag in presence of Na_2CO_3 [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21(8): 1860–1867.
- [9] VANVUUREN C P J, STANDER P P. The oxidation of FeV_2O_4 by oxygen in a sodium carbonate mixture [J]. *Mineral Engineering*, 2001, 14: 803–808.
- [10] CHEN Hou-sheng. Extraction of vanadium pentoxide from vanadium slag by lime calcination [J]. *Iron Steel Vanadium Titanium*, 1992, 13(6): 1–9. (in Chinese)
- [11] SADYKHOV G B, GONCHAROV K V, GONCHARENKO T V, OLYUNINA T V. Phase transformations during the oxidation of calcium-containing titanium–vanadium slags and their influence on the formation of calcium vanadates [J]. *Russian Metallurgy (Metally)*, 2013, 2013(2): 161–168.
- [12] JENA B C, DRESLER W, REILLY I G. Extraction of titanium, vanadium and iron from titanomagnetite deposits at pipestone lake, Manitoba, Canada [J]. *Mineral Engineering*, 1995, 8: 159–168.
- [13] LI Q G, ZHANG Q X, ZENG L, XIAO L S, YANG Y N. Removal of vanadium from ammonium molybdate solution by ion exchange [J]. *Transactions of Nonferrous Metals Society of China*, 2009, 19: 735–739.
- [14] GUPTA C K. Extractive metallurgy of niobium, tantalum and vanadium [J]. *International Metals Reviews*, 1984, 29: 405–444.
- [15] LI Hong, WANG Wan-jun, LI Jing-jie, WANG Xin, ZHOU Rong-zhang. Extracting vanadium with alkaline leaching after blowing oxygen to hot vanadium slag [J]. *Journal of University of Science and Technology Beijing*, 1994, 16(1): 14–19. (in Chinese)
- [16] LI Hong, SONG Wen-chen, NIU Si-tong, NIU Shi-zhen, GUO Luo-fang. A method of energy conservation and emissions reduction to treat molten vanadium bearing slag: Chinese Patent, ZL201110044380.5 [P]. 2012. (in Chinese)
- [17] SONG Wen-chen, LI Hong. A new process for vanadium extraction from molten vanadium slag by direct oxidation and sodium activating method [J]. *Iron Steel Vanadium Titanium*, 2012, 33(6): 1–5. (in Chinese)
- [18] HUANG Dao-xin. Vanadium extraction and steelmaking [M]. Beijing: Metallurgical Industry Press, 2000: 17–22. (in Chinese)
- [19] MAHDAVIAN A, SHAFYEI A, KESHAVARZ ALAMDARI E, HAGHSHENAS D F. Recovery of vanadium from Esfahan steel company steel slag; optimizing of roasting and leaching parameters [J]. *International Journal of ISSI*, 2006, 3: 17–21.
- [20] AARABI-KARASGANI M, RASHCHI F, MOSTOUFI N, VAHIDI E. Leaching of vanadium from LD converter slag using sulfuric acid [J]. *Hydrometallurgy*, 2010, 102: 14–21.
- [21] LI X S, XIE B. Extraction of vanadium from high calcium vanadium slag using direct roasting and soda leaching [J]. *International*

- Journals of Minerals, Metallurgy and Materials, 2012, 19: 595–601.
- [22] LI H R, FENG Y L, LIANG J Y, LUO X B, DU Z W. Vanadium recovery from clay vanadium mineral using an acid leaching method [J]. Rare Metals, 2008, 27: 116–120.
- [23] MAZUREK K. Recovery of vanadium, potassium and iron from a spent vanadium catalyst by oxalic acid solution leaching, precipitation and ion exchange processes [J]. Hydrometallurgy, 2013, 103: 26–31.
- [24] WANG Han-zhou. Slag analysis [M]. Beijing: Science Press, 2006: 753–755. (in Chinese)
- [25] MITTELSTADT R, SCHWERDTFEGER K. Dependence of the oxidation state of vanadium on the oxygen pressure in melts of VO_x , $\text{Na}_2\text{O}-\text{VO}_x$, and $\text{CaO}-\text{SiO}_2-\text{VO}_x$ [J]. Metallurgical Transactions B, 1990, 21: 111–120.
- [26] COLTON R J, GUZMAN A M, RABALAIS J W. Electrochromism in some thin-film transition-metal oxides characterized by X-ray electron spectroscopy [J]. Journal of Applied Physics, 1978, 49: 409–416.
- [27] CORNAGLIA L M, LOMBARDO E A. XPS studies of the surface oxidation states on vanadium–phosphorus–oxygen (VPO) equilibrated catalysts [J]. Applied Catalysis A: General, 1995, 127: 125–138.
- [28] WU Xiao-wei, ZHU Fa-hua, YANG Jin-tian. Measurements of emission factors of greenhouse gas (CO_2 , N_2O) from thermal power plants in China [J]. Research of Environmental Sciences, 2010, 23(2): 170–176. (in Chinese)
- [29] ZHANG Jia-yun. Physical chemistry in metallurgy [M]. Beijing: Metallurgical Industry Press, 2004: 324. (in Chinese)
- [30] FENG Ju-he. Steelmaking design principle [M]. Beijing: Chemical Industry Press, 2008: 22. (in Chinese)

熔融钒渣纯氢氧化钙化提钒

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摘要: 在实验室条件下对熔融态钒渣直接氢氧化钙化提钒新工艺进行研究。在反应过程中利用纯氢氧化钙, CaO 作为添加剂, 硫酸浸出熟料。采用 XRD、XPS、SEM 及 EDS 等手段对钒渣熟料进行分析, 考察不同 $\text{CaO}/\text{V}_2\text{O}_5$ 质量比与硫酸浓度对熟料中钒浸出的影响, 并与现行焙烧工艺在能耗方面进行对比。结果表明: 钒渣熟料中形成了钒的富集相, 钒渣的氢氧化钙化产物主要为 CaV_2O_5 和 $\text{Ca}_2\text{V}_2\text{O}_7$, 并对钒酸钙的形成机理进行了阐释; XRD 和 XPS 分析得出熔渣中钒的氧化反应在供氧充足的情况下存在一定限制, CaO 的增加能促进五价钒在熔渣中的稳定; 在优化的实验条件下 ($\text{CaO}/\text{V}_2\text{O}_5$ 质量比 0.6, 粒度 120~150 μm , 浸出时间 2 h, 浸出温度 90 $^\circ\text{C}$, 液固比 5:1 mL/g, H_2SO_4 浓度 20%, 搅拌强度 500 r/min), 钒的浸出率能达到 90%; 能耗计算得到每处理 1000 kg 钒渣, 利用新工艺可以节约能量 1.85×10^6 kJ。实验与计算结果验证新工艺是一种节能减排的提钒手段。

关键词: 熔融态钒渣; 氢氧化钙; 氧化; 酸浸; 钒回收; 节能

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