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A NEW PROCESS FOR EXTRACTING VANADIUM BY DIRECT CALCIFICATION USING THE HEAT OF MOLTEN VANADIUM SLAG

J.-W. Qu [a,b], T.-A. Zhang [b*], G.-Z. Lv [b], Y. Chen [b]

[a] Guangxi Key Laboratory of Calcium Carbonate Resources Comprehensive Utilization, Hezhou University, Hezhou, China
[b] Key Laboratory of Ecological Utilization of Multi-Metal Intergrown Ores of the Ministry of Education, School of Metallurgy, Northeastern University, Shenyang, China

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Abstract

A novel technology for extracting vanadium from molten converter vanadium slag was studied at the laboratory scale by oxidation and calcification. The effect of the cooling method, CaO addition, and reaction time on the phases of calcified vanadium slag was studied. Under the action of oxygen and CaO, the molten vanadium slag underwent calcification reaction to form acid-soluble calcium vanadate phase and the feasibility of its main chemical reaction was calculated by Factsage8.1. The calcified vanadium slag was leached by H_2SO_4 *solution and characterized by the XRF, XRD, SEM, and EDS techniques. Compared with the traditional process, the new process saved much energy, and it was faster and more efficient. The XRD results showed that* CaV_2O_5, $Ca_7V_4O_{17}$, *and* $Ca_3V_2O_8$ *were gradually formed in the molten vanadium slag with increasing CaO addition. However, when too much CaO was added,* Ca_2SiO_4 *and* $CaTiO_3$ *were also formed. These phases wrapped part of the vanadium and reduced the leaching rate of vanadium. When the mass ratio of Ca to V was 0.75, under the optimal acid leaching conditions (particle size of calcified vanadium slag less than 0.075 mm, leaching temperature 90 ℃,* H_2SO_4 *concentration 200 g.L*$^{-1}$*, liquid-to-solid ratio 6:1 ml.g*$^{-1}$*, leaching time 60 min, and stirring speed 300r.min*$^{-1}$*), the leaching rate of vanadium from calcified vanadium slag could exceed 90%. The new process not only saved energy and reduced emissions, but also reached the average level of the existing vanadium extraction process.*

Keywords: *Molten vanadium slag; CaO; Oxidation; Calcification; Leaching efficiency*

1. Introduction

As an important strategic metal, vanadium is known as modern industrial monosodium glutamate, and it has been widely used in many fields such as steel, aerospace, automobiles, bridges and new energy [1-3]. The main mineral resource of vanadium is vanadium-titanium magnetite, in which titanium, iron, and vanadium are symbiotic [4, 5]. At present, the main process for extracting vanadium from vanadium-titanium magnetite is as follows: Vanadium-titanium magnetite undergoes beneficiation to obtain high-vanadium iron concentrate; the iron concentrate is smelted in a blast furnace to produce vanadium-containing molten iron; the vanadium-containing molten iron is roasted in a converter to obtain vanadium slag and semi steel [6-8]. This vanadium slag is generally called converter vanadium slag.

The traditional process of extracting vanadium from converter vanadium slag includes cooling, crushing, and ball grinding. Sodium salts such as Na_2CO_3, NaCl, and Na_2SO_4 are mixed with vanadium slag and then heated to 800 °C in a rotary kiln or multibed furnace [9, 10]. After the reaction, vanadium is converted into sodium vanadate, which is easily soluble in water. Vanadium enters the water leaching solution after leaching. After adding ammonium salt and adjusting the pH value, vanadium is precipitated in the form of ammonium metavanadate or ammonium polyvanadate. Ammonium vanadate can be decomposed by roasting to obtain V_2O_5 [11, 12].

Sometimes converter vanadium slag and calcium salt are mixed and heated to 900 °C in an oxidizing atmosphere, and vanadium is converted into calcium vanadate, which is easily soluble in acid. The calcified vanadium slag is leached by acid to make vanadium enter the acid leaching solution [13-16]. Finally, after removing impurities in the acid leaching solution and adjusting the pH value, ammonium polyvanadate can be obtained, and high-purity V_2O_5 can be obtained by calcination [17-19].

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[*] *Corresponding author: zta2000@163.net*

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The traditional process of extracting vanadium from converter vanadium slag is cooling, crushing, ball grinding, mixing and pelletizing, and then the pellets are roasted and leached to extract vanadium [20-21]. In other words, the heat of the vanadium slag from the converter is wasted, and then much energy is required to heat it to a certain temperature. Therefore, this study will utilize the heat of converter vanadium slag to turn the vanadium slag into a molten state, and then add CaO while blowing oxygen. After the vanadium slag undergoes the calcification reaction, the calcium vanadate phase is formed. The new process studied the effect of the cooling method of calcified vanadium slag, CaO addition, and reaction time on the phases of calcified vanadium slag, and then studied the particle size of the calcified vanadium slag, leaching temperature, H_2SO_4 concentration, and liquid to solid ratio on the leaching rate of vanadium [22].

2. Experimental

2.1. Materials and analysis

The converter vanadium slag used in this study was obtained from Pangang Group, Sichuan Province, China. To ensure the uniformity of the sample in each experiment, the original samples were crushed and ground to less than 0.15 mm. Its semi quantitative composition was analyzed by X-ray fluorescence (XRF-1800, Shimadzu, Japan) and the results are given in Table 1.

The X-ray diffraction (XRD) pattern analysis of converter vanadium slag was recorded by a Rigaku D/MAX 2200 diffractometer with Cu Ka radiation at 40 kV and 20 mA using a scan speed of 5°min^{-1} in 2θ ranges from 10° to 90°. The XRD pattern analysis of converter vanadium slag was shown in Fig.1. As shown in Fig. 1, the main vanadium-containing phase in the converter vanadium slag was the spinel phase $[(Mn,Fe)(V,Cr)_2O_4]$, in which Cr and Mn replaced part of V and Fe in the crystal lattice, and the spinel phase was hard in texture and difficult to completely leach. In addition, there were olivine phase (Fe_2SiO_4), titanomagnetite phase ($Fe_{2.5}Ti_{0.5}O_4$), and magnetite phase (Fe_3O_4) in the converter vanadium slag.

The surface morphology and element composition of converter vanadium slag and calcified vanadium slag were examined by a scanning electron microscopy (SEM, JSM−6480 LV, Japan) equipped with energy dispersive spectroscope (EDS, Noran System six, American). The surface morphology of converter vanadium slag was shown in Fig.2. As shown in Fig.2, the major phases in converter vanadium slag were vanadium-bearing spinel and olivine.

Table 1. *Main chemical compositions of converter vanadium slag (mass fraction, %)*

Fe_2O_3	SiO_2	V_2O_5	TiO_2	Al_2O_3	MnO	MgO	Cr_2O_3	CaO	Na_2O
39.51	13.70	14.00	12.60	4.63	8.72	2.27	2.47	1.65	0.32

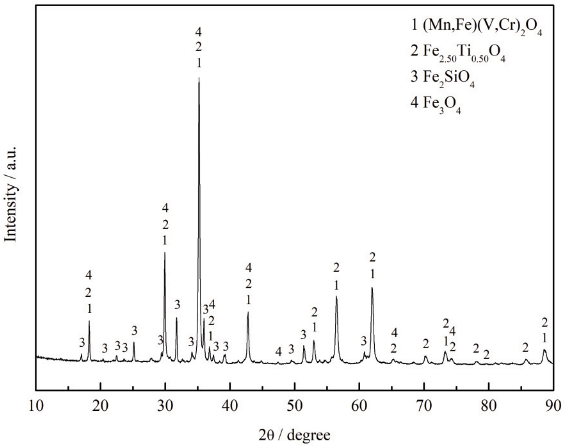
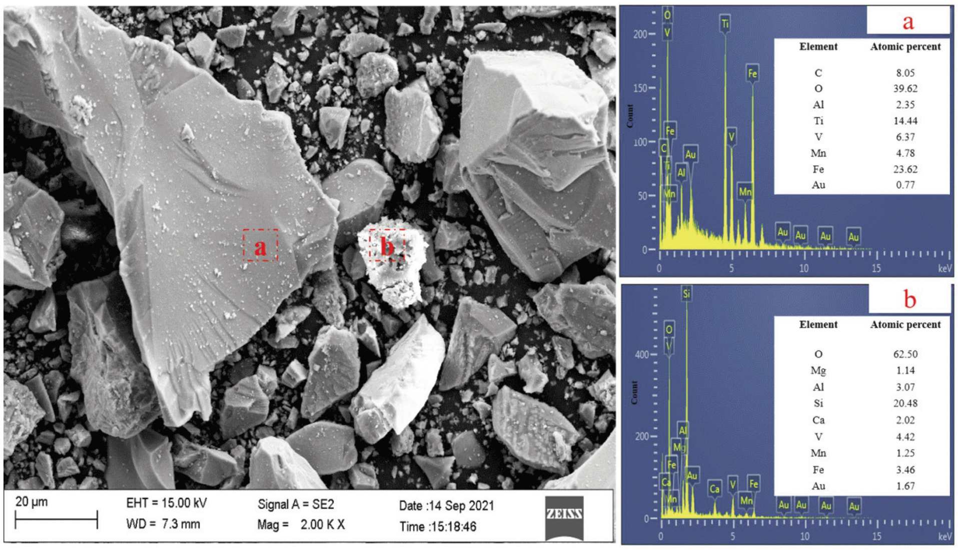


Figure 1. *XRD pattern of converter vanadium slag*



Element	Atomic percent
C	8.05
O	39.62
Al	2.35
Ti	14.44
V	6.37
Mn	4.78
Fe	23.62
Au	0.77

Element	Atomic percent
O	62.50
Mg	1.14
Al	3.07
Si	20.48
Ca	2.02
V	4.42
Mn	1.25
Fe	3.46
Au	1.67

Figure 2. *SEM image of converter vanadium slag*

2.2. Method

The comparison between the new process and traditional process was shown in Fig. 3. The new process included calcification and acid leaching. The new process saved considerable energy consumption, and was faster and more efficient.

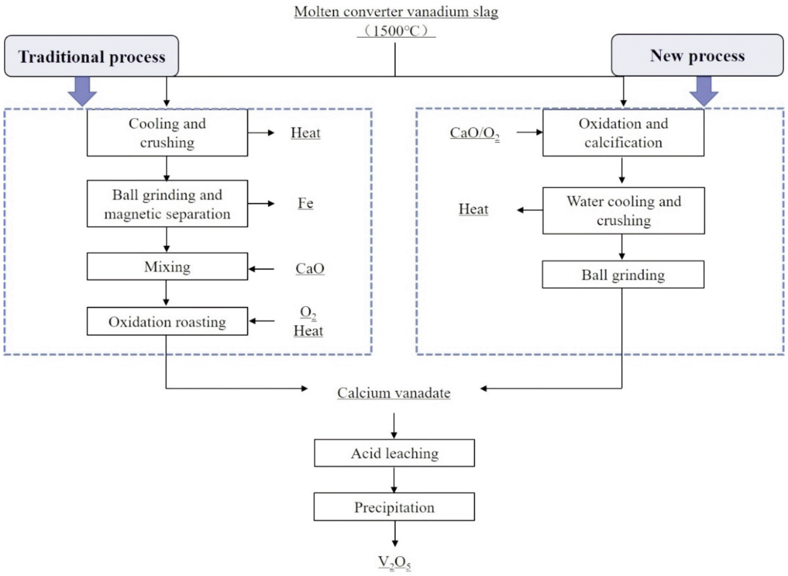


Figure 3. *Comparison of flow chart between new process and traditional process*

2.2.1. Oxidation and calcification

The experimental temperature was 1500 °C to keep the vanadium slag in a completely molten state. Pure oxygen was used to create an oxidizing atmosphere. A furnace with silicon molybdenum rods as heating elements was used to melt vanadium slag. The temperature of the furnace was controlled within ±5 °C by a thermocouple that was placed at the bottom of the protective crucible.

The schematic diagram of the whole experimental apparatus was shown in Fig. 4. In each experiment, 100 g of vanadium slag was put into a corundum crucible (Φ48 mm×120 mm), and this crucible was placed in a corundum sleeve (Φ70 mm×700 mm) in the furnace. Then the furnace was heated to 1500 °C at a rate of 10 °C/min in a protective atmosphere. When the vanadium slag was completely melted, a certain amount of CaO was added to the corundum

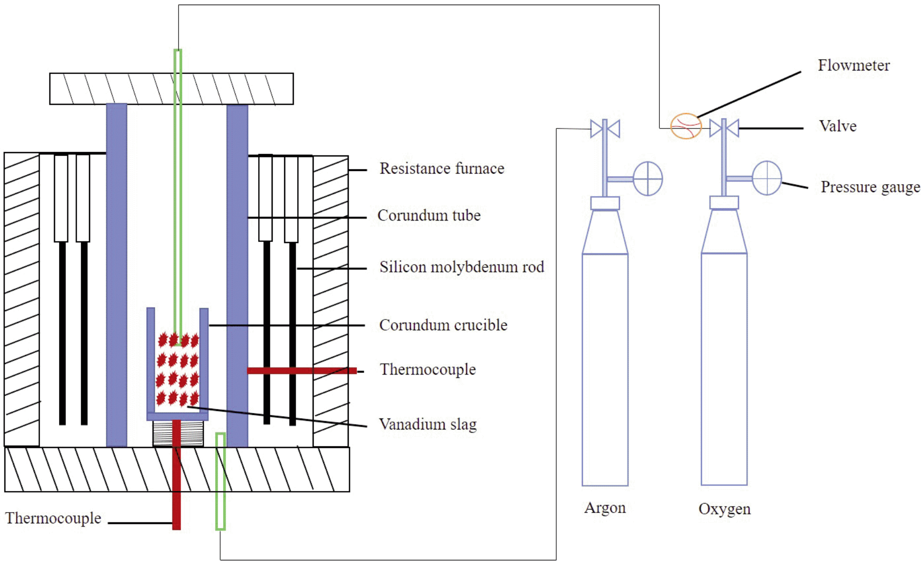


Figure 4. *Schematic diagram of the experimental apparatus for molten converter vanadium slag*

crucible, and then the pure oxygen was blown into the molten vanadium slag immediately by a single-hole alumina tube (Φ5 mm×1000 mm), which could help the process of oxidation reaction. The oxygen flow rate was 1 L/min and the reaction time was 10 min.

After the calcification reaction of molten vanadium slag, the crucible was removed and cooled to room temperature with water. Then the crucible was crushed to remove the calcified vanadium slag, and finally a planetary ball mill was used to make the particle size of the calcified vanadium slag less than 0.075 mm. XRF, XRD, SEM, and EDS were used to analyze the composition, phase and surface morphology of the calcified vanadium slag.

2.2.2. Acid leaching

The leaching experiments were carried out in a water bath that could be heated and stirred. In each leaching experiment, 10 g of the calcified vanadium slag was leached in sulfuric acid solution (200 g.L^{-1}) at 90 °C for 60 min. The ratio of liquid to solid (L/S ratio) was 6:1 (mL/g), and the stirring speed was 300 r.min^{-1}. In order to obtain the best leaching rate of vanadium, the acid leaching experiment investigated the influence of the particle size of calcified vanadium slag, leaching temperature, H_2SO_4 concentration, and liquid to solid ratio. After each leaching test, the leaching solution was separated via vacuum filtration, and the leaching residue was washed with deionized water. The vanadium content in the leaching residue was determined by ICP, which was used to calculate the leaching rate of vanadium.

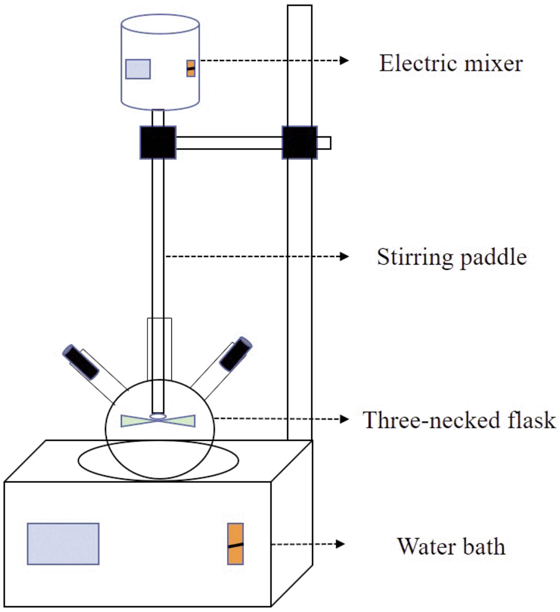


Figure 5. *Schematic diagram of the experimental apparatus for calcified vanadium slag*

3. Results and discussion

3.1. Thermodynamic feasibility of the main reactions during calcification

When CaO was added to the molten vanadium slag, CaO reacted with V_2O_5 to form various calcium vanadate. The thermodynamic feasibility of these reactions was shown in Fig. 6. The thermodynamic data were derived from Factsage8.1. It could be seen from Fig. 6 that the ΔG^0 of the reaction between CaO and V_2O_5 was less than 0. The generation trend of the three types of calcium vanadate was $Ca_3V_2O_8 > Ca_2V_2O_7 > CaV_2O_6$. However, in actual situations, due to the difference in the CaO addition, all three types of calcium vanadate might exist.

When CaO was added to the molten vanadium slag, various reactions occurred between CaO and other oxides. The thermodynamic feasibility of these reactions was shown in Fig. 7. It could be seen from Fig. 7 that SiO_2, Al_2O_3, TiO_2, and Fe_2O_3 reacted with CaO, among which calcium silicate was the most easily generated, followed by calcium titanate, and finally calcium ferrite. In addition, calcium aluminosilicate would also be generated.

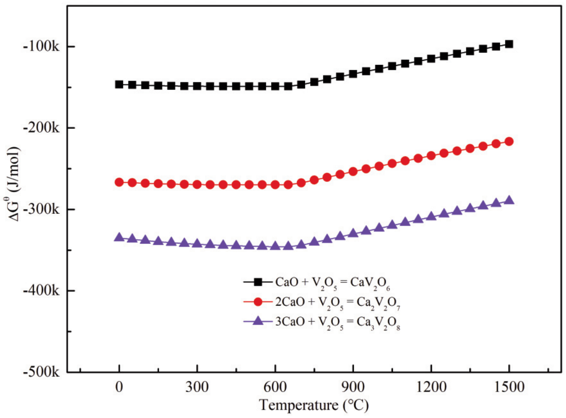


Figure 6. *The ΔG^0-T relationship of reaction of V_2O_5 with CaO*

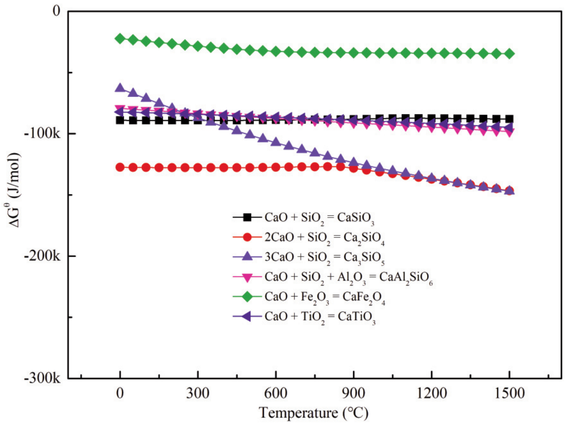


Figure 7. *The ΔG^0-T relationship of reaction of other oxides with CaO*

3.2. Phase diagram analysis of vanadium slag at 1000~1500 °C

Figure 8 was the ternary phase diagram of CaO-SiO_2-V_2O_5 at 1000~1500 °C. The phase in the molten slag changed with the composition. When the content of CaO or SiO_2 was more than 70%, the slag mainly existed as CaO or SiO_2. When the content of V_2O_5 was more than 50%, the slag mainly existed as calcium vanadate, calcium silicate, and liquid phase. The calcium silicate phase was mainly $CaSiO_3$, Ca_2SiO_4, Ca_3SiO_5, and $Ca_3Si_2O_7$, the calcium vanadate phase was mainly CaV_2O_6, $Ca_2V_2O_7$, and $Ca_3V_2O_8$. In addition, with the change of the composition of molten vanadium slag, the minimum melting temperature was 754.80 °C, and the maximum melting temperature was 3060.63 °C.

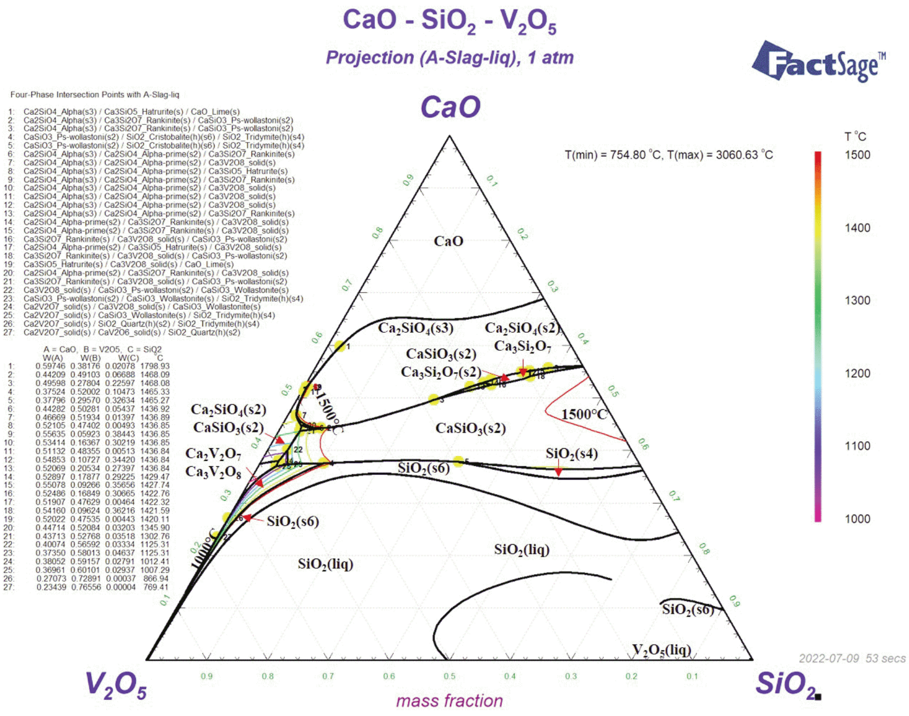
3.3. Melting experiment

3.3.1. Effect of cooling methods

Table 2 shows the composition of the calcified vanadium slag obtained by different cooling methods. The Al_2O_3 content in the air-cooled vanadium slag was higher. The reason may be that the time of air cooling was longer than that of water cooling, so the aluminum in the corundum crucible gradually entered the vanadium slag.

Figure 9 shows the XRD patterns of calcified vanadium slag obtained by different cooling methods. The phases of the air-cooled slag were mainly $CaAl_2Si_2O_8$, Fe_2SiO_4, and Ca_2SiO_4. In addition, there were small amounts of $Mn_2V_2O_7$ and CaV_2O_5. There were no $CaAl_2Si_2O_8$ and Ca_2SiO_4 phases in the water-cooled slag, but there were more calcium vanadate phases ($Ca_7V_4O_{17}$ and $Ca_3V_2O_8$). Therefore, to make more calcium vanadate appear in the vanadium slag, water cooling was selected as the cooling method of the molten vanadium slag.

Figure 10 shows the SEM image and EDS analysis results of the calcified vanadium slag with water cooling. Combining the XRD and EDS analysis results, it can be seen that a) was the calcium vanadium phase, b) was the ilmenite phase, and c) was the calcium silicate phase. The carbon was derived from the conductive glue, while the aurum was derived from the SEM sample preparation process.



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Four-Phase Intersection Points with A-Slag-liq

 1:  Ca2SiO4_Alpha(s3) / Ca3SiO5_Hatrurite(s) / CaO_Lime(s)
 2:  Ca2SiO4_Alpha(s3) / Ca3Si2O7_Rankinite(s) / CaSiO3_Ps-wollastoni(s2)
 3:  Ca2SiO4_Alpha(s3) / Ca3Si2O7_Rankinite(s) / CaSiO3_Ps-wollastoni(s2)
 4:  CaSiO3_Ps-wollastoni(s2) / SiO2_Cristobalite(h)(s6) / SiO2_Tridymite(h)(s4)
 5:  CaSiO3_Ps-wollastoni(s2) / SiO2_Cristobalite(h)(s6) / SiO2_Tridymite(h)(s4)
 6:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s)
 7:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3V2O8_solid(s)
 8:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3SiO5_Hatrurite(s)
 9:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s)
10:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3V2O8_solid(s)
11:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3V2O8_solid(s)
12:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3V2O8_solid(s)
13:  Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s)
14:  Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s)
15:  Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s)
16:  Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s) / CaSiO3_Ps-wollastoni(s2)
17:  Ca2SiO4_Alpha-prime(s2) / Ca3SiO5_Hatrurite(s) / Ca3V2O8_solid(s)
18:  Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s) / CaSiO3_Ps-wollastoni(s2)
19:  Ca3SiO5_Hatrurite(s) / Ca3V2O8_solid(s) / CaO_Lime(s)
20:  Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s)
21:  Ca3Si2O7_Rankinite(s) / Ca3V2O8_solid(s) / CaSiO3_Ps-wollastoni(s2)
22:  Ca3V2O8_solid(s) / CaSiO3_Ps-wollastoni(s2) / CaSiO3_Wollastonite(s)
23:  CaSiO3_Ps-wollastoni(s2) / CaSiO3_Wollastonite(s) / SiO2_Tridymite(h)(s4)
24:  Ca2V2O7_solid(s) / Ca3V2O8_solid(s) / CaSiO3_Wollastonite(s)
25:  Ca2V2O7_solid(s) / CaSiO3_Wollastonite(s) / SiO2_Tridymite(h)(s4)
26:  Ca2V2O7_solid(s) / SiO2_Quartz(h)(s2) / SiO2_Tridymite(h)(s4)
27:  Ca2V2O7_solid(s) / CaV2O6_solid(s) / SiO2_Quartz(h)(s2)

          A = CaO,  B = V2O5,  C = SiO2
          W(A)     W(B)     W(C)      °C
 1:     0.59746  0.38176  0.02078  1798.93
 2:     0.44209  0.49103  0.06688  1468.09
 3:     0.49598  0.27804  0.22597  1468.08
 4:     0.37524  0.52002  0.10473  1465.33
 5:     0.37796  0.29570  0.32634  1465.27
 6:     0.44282  0.50281  0.05437  1436.92
 7:     0.46669  0.51934  0.01397  1436.89
 8:     0.52105  0.47402  0.00493  1436.85
 9:     0.55635  0.05923  0.38443  1436.85
10:     0.53414  0.16367  0.30219  1436.85
11:     0.51132  0.48355  0.00513  1436.84
12:     0.54853  0.10727  0.34420  1436.84
13:     0.52069  0.20534  0.27397  1436.84
14:     0.52897  0.17877  0.29225  1429.47
15:     0.55078  0.09266  0.35656  1427.74
16:     0.52486  0.16849  0.30665  1422.76
17:     0.51907  0.47629  0.00464  1422.32
18:     0.54160  0.09624  0.36216  1421.59
19:     0.52022  0.47535  0.00443  1420.11
20:     0.44714  0.52084  0.03203  1345.90
21:     0.43713  0.52768  0.03518  1302.76
22:     0.40074  0.56592  0.03334  1125.31
23:     0.37350  0.58013  0.04637  1125.31
24:     0.38052  0.59157  0.02791  1012.41
25:     0.36961  0.60101  0.02937  1007.29
26:     0.27073  0.72891  0.00037   866.94
27:     0.23439  0.76556  0.00004   769.41
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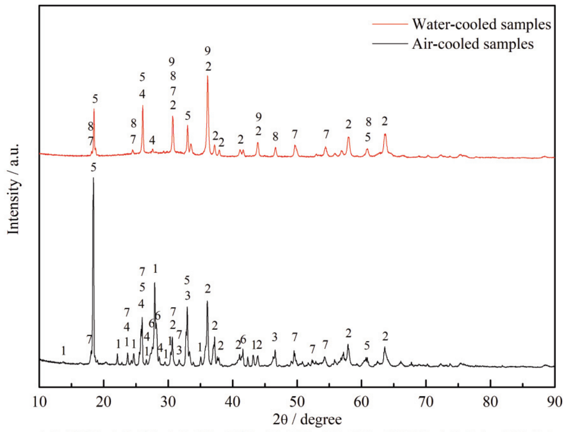
Figure 8. *Phase diagram analysis of vanadium slag at 1000~1500℃*

Table 2. *Main chemical composition of calcified vanadium slag with different cooling methods (mass fraction, %)*

	Na_2O	MgO	Al_2O_3	SiO_2	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	Fe_2O_3
Air cooling	0.59	1.22	19.8	13.7	6.25	10.9	11.0	1.20	5.92	28.8
Water cooling	0.76	1.32	14.1	12.7	6.13	10.3	11.3	1.02	6.83	32.2



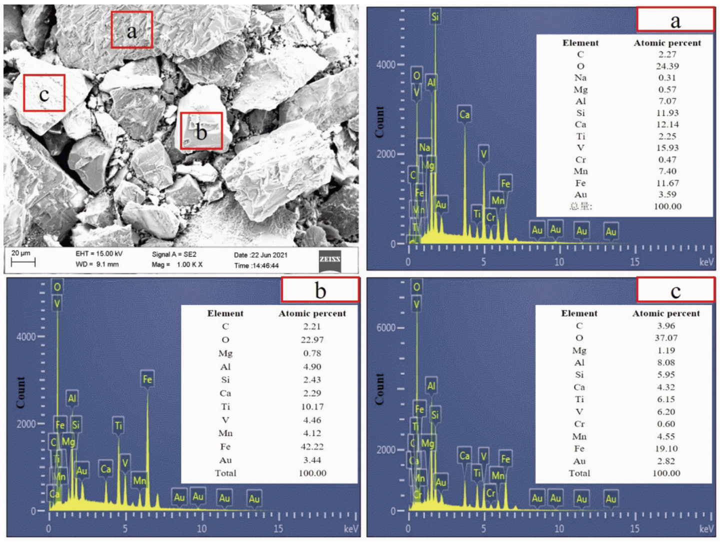
1 $CaAl_2Si_2O_8$; 2 Fe_2SiO_4; 3 Ca_2SiO_4; 4 SiO_2; 5 Fe_2TiO_5; 6 $Mn_2V_2O_7$; 7 CaV_2O_5; 8 $Ca_7V_4O_{17}$; 9 $MnAl_2O_4$

Figure 9. *XRD pattern of the calcified vanadium slag with different cooling methods*

3.3.2. Effect of CaO addition

Figure 11 shows the XRD patterns of calcified vanadium slag with different CaO additions. The XRD results revealed that the main vanadium-containing phases in calcified vanadium slag were CaV_2O_5, CaV_2O_6, $Ca_7V_4O_{17}$, and $Ca_3V_2O_8$. When the *mCa/mV* was 0.25, only CaV_2O_5 was formed in the calcified vanadium slag. As the *mCa/mV* increased to 0.75, CaV_2O_6, $Ca_7V_4O_{17}$, and $Ca_3V_2O_8$ were formed in the calcified vanadium slag. In addition, when the *mCa/mV* was 1.00, $CaCO_3$ reacted with SiO_2 and TiO_2 to form Ca_2SiO_4 and $CaTiO_3$.

Figure 12 shows that when the *mCa/mV* was 0.8, the leaching rate of vanadium from calcified vanadium slag was the highest. With increasing the *mCa/mV*, the leaching rate of vanadium slowly decreased. The reason may be that when the addition

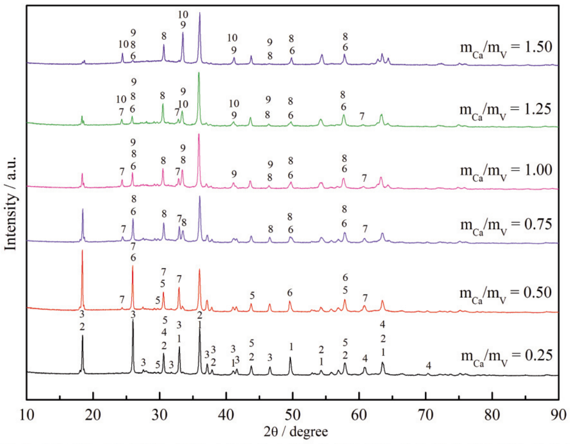


Element	Atomic percent
C	2.27
O	24.39
Na	0.31
Mg	0.57
Al	7.07
Si	11.93
Ca	12.14
Ti	2.25
V	15.93
Cr	0.47
Mn	7.40
Fe	11.67
Au	3.59
总量:	100.00

Element	Atomic percent
C	2.21
O	22.97
Mg	0.78
Al	4.90
Si	2.43
Ca	2.29
Ti	10.17
V	4.46
Mn	4.12
Fe	42.22
Au	3.44
Total	100.00

Element	Atomic percent
C	3.96
O	37.07
Mg	1.19
Al	8.08
Si	5.95
Ca	4.32
Ti	6.15
V	6.20
Cr	0.60
Mn	4.55
Fe	19.10
Au	2.82
Total	100.00

Figure 10. *SEM image and EDS analysis results of the calcified vanadium slag with water cooling*



1 Fe_2O_3;2 Fe_2SiO_4;3 $FeAlTiO_5$;4 SiO_2;5 CaV_2O_5;6 CaV_2O_6;7 $Ca_7V_4O_{17}$;8 $Ca_3V_2O_8$;9 Ca_2SiO_4;10 CaT

Figure 11. *XRD patterns of calcified vanadium slag with different mCa/mV*

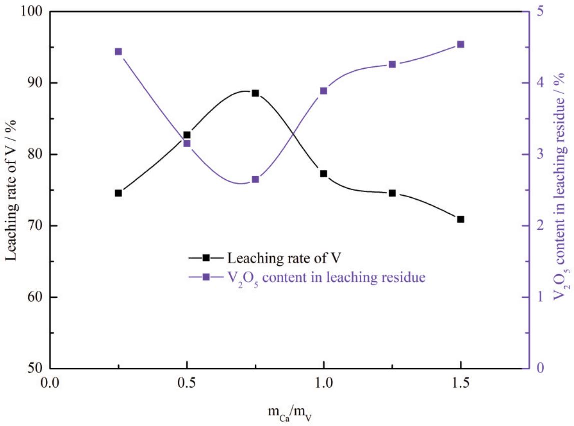


Figure 12. *Effect of mCa/mV on the leaching rate of vanadium*

amount of CaO was too high, the generated Ca_2SiO_4 and $CaTiO_3$ would wrap part of vanadium and hinder the leaching of vanadium.

Figure 13 shows SEM images of calcified vanadium slag with different CaO additions. The corresponding EDS analysis results are shown in Table 3. The calcified vanadium slag had an irregular shape distribution and different particle sizes. Combining the EDS analysis results and the phase analysis results, the main phases in the calcified vanadium slag were ilmenite, calcium vanadate, and calcium silicate. With the increase of CaO addition, the spinel phase gradually disappeared, and the phases of calcium vanadate and calcium silicate gradually increased.

3.3.3. *Effect of reaction time*

Figure 14 shows the XRD patterns of the calcified vanadium slag at different reaction time. The XRD results revealed that when the reaction time was 1 min, the major phases in calcified vanadium slag were Fe_3O_4, Fe_2O_3, $(Ti_{0.7}V_{0.3})_2O_3$, $CaSiO_3$, and $Ca_3V_2O_8$. When the reaction time was 5 min, CaV_2O_5 and $Ca_3V_2O_8$ were formed in the calcified vanadium slag. When the reaction time exceeded 5 minutes, the phases of the calcified vanadium slag were basically unchanged. It can also be seen from Fig. 15 that when the reaction time was 1 min, the leaching rate of vanadium was approximately 70%. When the reaction time exceeded 5 minutes, the leaching rate of V increased to 90%.

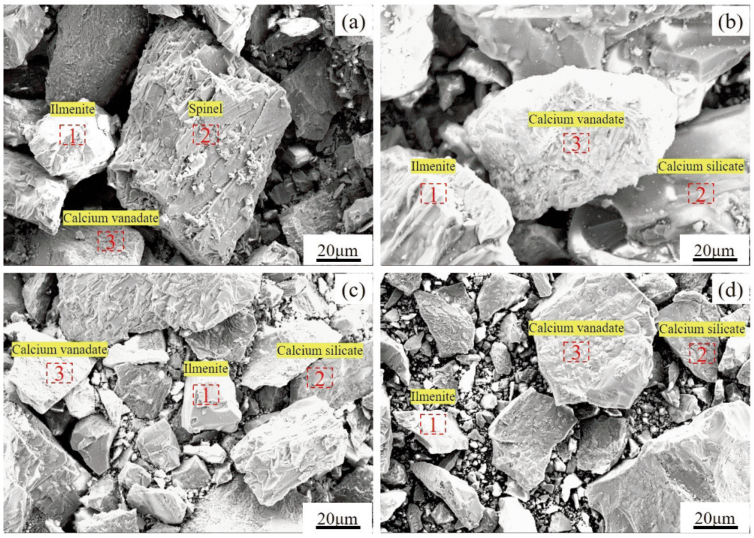


Figure 13. *SEM images of calcified vanadium slag with different mCa/mV: (a) 0.25; (b) 0.75; (c) 1.25; (d) 1.50*

Table 3. *EDS analysis results of calcified vanadium slag with different mCa/mV (mass fraction, %)*

No.	O	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe
a-1	30.52	-	5.57	-	0.82	10.13	5.16	2.39	7.77	33.65
a-2	29.09	2.84	2.28	0.60	-	1.46	12.06	3.96	8.17	33.49
a-3	16.42	1.00	6.88	11.94	5.39	2.35	18.24	-	14.56	23.03
b-1	16.84	0.21	1.29	0.93	3.05	10.54	6.33	1.91	5.98	49.84
b-2	31.74	0.77	7.94	12.27	8.03	6.41	5.04	-	8.33	13.62
b-3	35.74	0.56	3.24	8.85	14.06	2.41	15.04	-	2.33	12.62
c-1	22.97	0.78	4.90	2.43	2.29	10.17	4.46	-	4.12	42.22
c-2	37.20	1.04	8.27	11.30	16.03	2.56	2.99	-	6.89	7.14
c-3	24.39	0.57	7.07	11.93	12.14	2.25	15.93	0.47	7.40	11.67
d-1	16.81	0.10	0.59	0.61	11.36	17.89	4.69	-	8.26	38.56
d-2	34.13	0.39	7.22	12.13	15.32	2.82	2.59	0.36	3.55	14.59
d-3	17.69	0.25	1.98	1.94	23.06	8.61	20.46	0.91	6.89	14.66

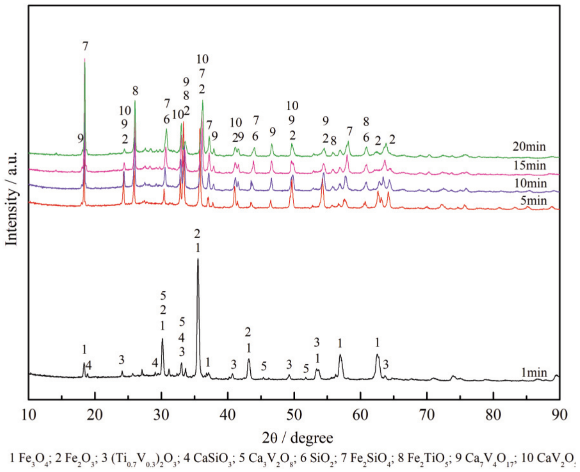


Figure 14. *XRD patterns of calcified vanadium slag with different reaction times*

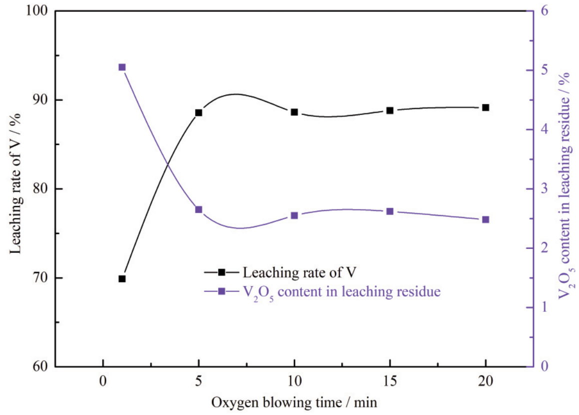


Figure 15. *Effect of reaction time on the leaching rate of vanadium*

3.4. Leaching

The molten vanadium slag underwent calcification to form calcified vanadium slag, in which most of the vanadium existed in the form of calcium vanadate, which was generally insoluble or slightly soluble in water, but soluble in acid. Since the solubility product of calcium sulfate was smaller than that of calcium vanadate, sulfuric acid was used to leach calcified vanadium slag, so that vanadium entered the leaching solution. The reactions that took place during acid leaching were as follows:

$$CaV_2O_6 + 2H_2SO_4 = CaSO_4 + (VO_2)_2SO_4 + 2H_2O$$

$$Ca_2V_2O_7 + H_2SO_4 = 2CaSO_4 + (VO_2)_2SO_4 + 3H_2O$$

$$Ca_3V_2O_8 + 4H_2SO_4 = 3CaSO_4 + (VO_2)_2SO_4 + 4H_2O$$

The main influencing factors in the acid leaching process were the particle size of the calcified vanadium slag, the concentration of sulfuric acid, the liquid-solid ratio, and the leaching temperature. The following are the results and discussions of the influence of these factors on vanadium extraction.

3.4.1. Effect of particle size of calcified vanadium slag

The experimental results of the effect of the particle size of calcified vanadium slag on the leaching efficiency of vanadium are shown in Fig. 16, which were obtained by leaching 10 g calcified vanadium slag in 200 g·L^{-1} H_2SO_4 solution with L/S ratio 10:1 ml·g^{-1} at different particle sizes for 60 min. The results showed that the leaching efficiency of vanadium increased with decreasing particle size. When the particle size of calcified vanadium slag was less than 0.075 mm, the leaching rate of vanadium could reach more than 90%. As the particle size decreased, the leaching rate of V did not change much. Therefore, the optimal particle size for extracting vanadium from calcified vanadium slag was less than 0.075 mm.

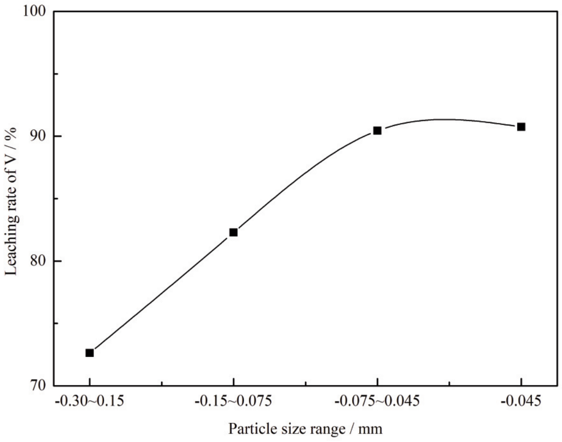


Figure 16. *Effect of the particle size of calcified vanadium slag on vanadium extraction*

3.4.2. Effect of leaching temperature

The experimental results of the effect of leaching temperature on the leaching efficiency of vanadium were obtained by leaching 10 g calcified vanadium slag in 200 g·L^{-1} H_2SO_4 solution with L/S ratio 10:1 ml·g^{-1} at different temperatures for 60 min. The results in Fig. 17 show that the leaching efficiency of vanadium increased with increasing leaching temperature. When the leaching temperature was 90 °C, the leaching efficiency of vanadium reached the maximum value. When the leaching temperature continued to increase, the leaching efficiency of vanadium did not change much. Therefore, to save energy, the optimal leaching temperature was chosen to be 90 °C.

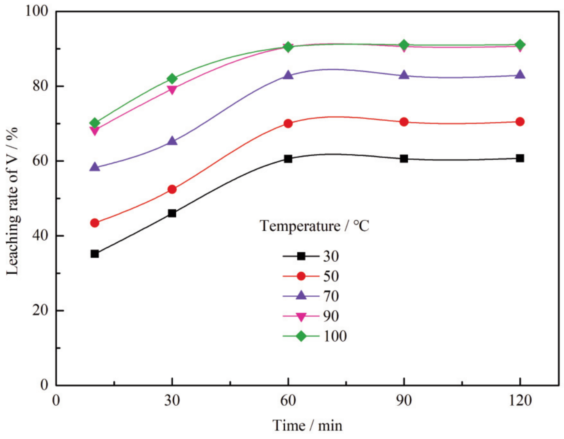


Figure 17. *Effect of leaching temperature on vanadium extraction*

3.4.3. Effect of H_2SO_4 concentration

The experimental results of the effect of H_2SO_4 concentration on the leaching efficiency of vanadium are shown in Fig. 18, which were obtained by leaching 10 g calcified vanadium slag in different concentrations of H_2SO_4 solution with L/S ratio 10:1 ml·g^{-1} at 90 °C for 60 min. The results showed that the leaching efficiency of vanadium increased with increasing H_2SO_4 concentration. When the H_2SO_4 concentration was 200 g·L^{-1}, the leaching efficiency of vanadium reached the maximum value (90.24%). Therefore, to obtain the maximum leaching efficiency of vanadium, the H_2SO_4 concentration was selected as 200 g·L^{-1}.

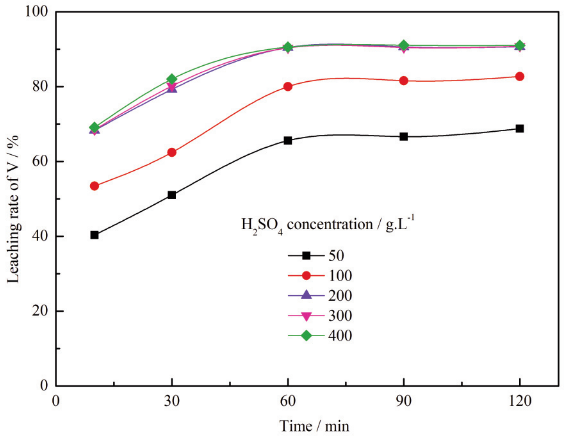


Figure 18. *Effect of H_2SO_4 concentration on vanadium extraction*

3.4.4. Effect of liquid to solid ratio

The experimental results of the effect of the liquid to solid ratio on the leaching efficiency of V are shown in Fig. 19, which were obtained by leaching 10 g calcified vanadium slag in 200 g·L^{-1} H_2SO_4 solution with different L/S ratios at 90 °C for 60 min. As shown in Fig. 19, the liquid to solid ratio significantly affected extraction of vanadium. The leaching efficiency of vanadium increased with increasing liquid to solid ratio. When the liquid to solid ratio was 6:1, the leaching efficiency of vanadium reached the maximum value. When the liquid to solid ratio increased to 10:1, the leaching efficiency of vanadium did not change much. Therefore, the best liquid to solid ratio should be selected as 6:1.

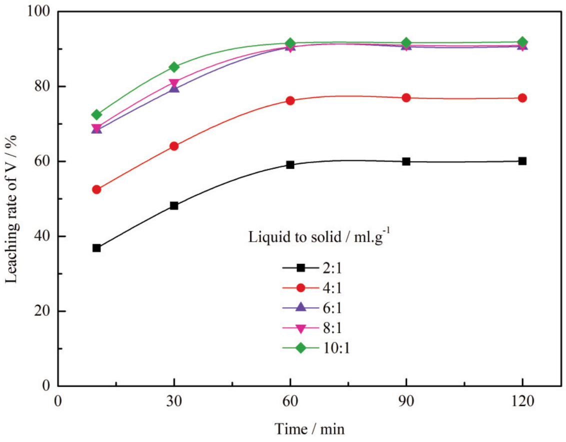


Figure 19. *Effect of solid to liquid ratio on vanadium extraction*

4. Conclusion

(1) Using the heat of the converter vanadium slag, oxygen was blown into the molten vanadium slag and CaO was added. After a certain reaction time, the calcified vanadium slag obtained after water cooling was leached by H_2SO_4 solution. Finally, the leaching rate of vanadium could reach more than 90%.

(2) After the molten vanadium slag was oxidized and calcified, the XRD results showed that a large amount of acid-soluble calcium vanadate phase was formed. The experiment investigated the effect of the cooling method of calcified vanadium slag, CaO addition and reaction time on the leaching rate of vanadium. When the *mCa/mV* was 0.75 and the reaction time was 5 minutes, the leaching rate of vanadium from calcified vanadium slag reached more than 90%.

(3) When the particle size of calcified vanadium slag was less than 0.075 mm, the leaching temperature was 90 °C, the H_2SO_4 concentration was 200 g·L^{-1}, and the liquid-to-solid ratio was 6:1 ml·g^{-1}, the leaching rate of V was 90.24% after leaching for 60 minutes.

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Author’s contributions

J. W. Qu designed this article and carried out all the experiments. T. Z. Zhang reviewed the article and agreed to submit it. All data reported in this study are available upon request by contact with the corresponding author and the first author.

Conflict of interest

The authors claim that they have no conflicts of interest.

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NOVI POSTUPAK ZA EKSTRAKCIJU VANADIJUMA DIREKTNOM KALCIFIKACIJOM KORIŠĆENJEM TOPLOTE RASTOPLJENE ŠLJAKE VANADIJUMA

J.-W. Qu [a,b], T.-A. Zhang [b*], G.-Z. Lv [b], Y. Chen [b]

[a] Glavna laboratorija u Guansiju za korišćenje resursa kalcijum karbonata, Univerzitet u Hedžou, Hedžou, Kina

[b] Glavna laboratorija za ekološku iskorišćenost ruda koje sadrže više metala pri Ministarstvu prosvete, Metalurški fakultet, Severoistočni univerzitet, Šenjang, Kina

Apstrakt

Nova tehnologija ekstrakcije vanadijuma iz rastopljene konvertorske šljake koristeći oksidaciju i kalcifikaciju proučavana je u laboratorijskim uslovima. Ispitivan je uticaj metode hlađenja, dodavanja CaO, kao i vreme reakcije na različite faze kalcifikovane šljake vanadijuma. Rastopljena šljaka je pod dejstvom kiseonika i CaO podvrgnuta reakciji kalcifikacije kako bi se formirala faza kalcijum vanadata koja je rastvorljiva u kiselini, a izvodljivost glavne hemijske reakcije izračunata je pomoću Factsage8.1. Kalcifikovana vanadijumska šljaka je lužena u prisustvu H_2SO_4, a zatim su urađene XRF, XRD, SEM i EDS analize. U poređenju sa tradicionalnim postupkom, novi postupak je uštedeo mnogo energije, a bio je i brži i efikasniji. Rezultati XRD analize su pokazali da se u rastopljenoj šljaci postepeno formiraju CaV_2O_5, $Ca_7V_4O_{17}$ i $Ca_3V_2O_8$ kada se poveća količina dodatog CaO. Međutim, ako se doda previše CaO, formiraju se i Ca_2SiO_4 i $CaTiO_3$. Ove faze su se delimično formirale oko vanadijuma i smanjile brzinu luženja. Kada je maseni odnos Ca i V iznosio 0,75, pod optimalnim uslovima kiselog luženja (veličina čestice kalcifikovane vanadijumske šljake manja od 0,075 mm, temperatura luženja 90 °C, koncentarcije H_2SO_4 200 $g.L^{-1}$, odnos tečno-čvrsto 6:1 $ml.g^{-1}$, vreme luženja 60 min i brzina mešanja 300 $r.min^{-1}$), procenat izluženja vanadijuma iz kalcifikovane šljake je prelazila 90%. Novi postupak je doprineo uštedi energije i smanjio emisiju, a dostigao je i prosečni nivo postojećeg procesa ekstrakcije vanadijuma.

Ključne reči: *Rastopljena vanadijumska šljaka; CaO; Oksidacija; Kalcifikacija; Luženje*