A novel method to extract vanadium from high-grade vanadium slag: non-salt roasting and alkaline leaching

Biao Liu [1], Lipeng Meng [2], Shili Zheng [1], Meng Li [3], Shaona Wang [1]

[1] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

[2] School of Metallurgy and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China;

[3] School of Metallurgy, Northeastern University, Shenyang, 110819, China

Corresponding author: shnwang@ipe.ac.cn (S. Wang)

Abstract: A new method using non-salt roasting-alkaline leaching to treat vanadium slag was proposed in this study. The V(III) in vanadium slag is oxidized to V(V) by roasting and the latter can be effectively leached out as vanadate by alkaline leaching. This method possesses distinct advantage of being able to treat high-grade vanadium slag. For the South Africa high-grade vanadium slag, the maximum vanadium recovery of 98% was achieved when the reaction conditions were roasting temperature of 850 °C, roasting time of 2 h, alkali concentration of 30 wt.%, leaching temperature of 210 °C, and leaching time of 2 h. The roasting and leaching mechanisms have been well elucidated based on the XRD and SEM analysis results. The phases transitions of vanadium slag were clearly presented. This work has laid the foundation for the industrial application of non-salt roasting-alkaline leaching and provided new insights into effective extraction of high-grade vanadium slag.

1. Introduction

Vanadium is a high melting point metal and is widely used in metallurgical industries due to its ability to enhance the mechanical properties such as tensile strength, hardness, and fatigue resistance of steels (Liao and Bo, 1985; Qiu et al., 2011). Iron and steel making industries consume about 85% of total vanadium production annually. There are about 65 types of vanadium-containing minerals in the world, and vanadium titanomagnetite is the main raw material for vanadium extraction, accounting for about 88% of vanadium production (Li et al., 2011b; Zhao, 1999). During steelmaking process, the vanadium titanomagnetite ore is oxidized and the vanadium is enriched into steel slag, which is called vanadium slag, and it is the direct source for vanadium extraction (Huang, 2000). Based on different vanadium slag production process, the grade of vanadium slag varies from 10% to 25% (Huang, 2000), which may affect the recovery of vanadium.

At present, sodium salt roasting is the most commonly used technology for the treatment of vanadium slag. In this process, vanadium slag is roasted with sodium salts (NaCl, NaCO$_3$ and Na$_2$SO$_4$) at a high temperature (750-850 °C) to produce sodium metavanadates which are then leached by water or acids. This is a well-developed technology, however, there are some environment and resource problems need to be concerned. Firstly, in the sodium salts roasting process, the decomposition of Na$_2$CO$_3$, Na$_2$SO$_4$ and NaCl produces a lot of harmful gases, such as Cl$_2$, SO$_2$ and HCl. These toxic gases would corrode equipment severely and are contaminative to the environment (Barolin, 1982; Moskalyk and Alfantazi, 2003). Secondly, the vanadium conversion rate of single roasting is only 65-85%, therefore, multiple roasting are always needed to attain a satisfactory recovery (Gu et al., 2007; Hukkanen and Walden, 1985; Shi et al., 2008; Wang, 2004). This is due to the fact that the added sodium salts would react and form low - melting point substances, such as

silicates, vanadates and chromates, which will wrap the un-reacted vanadium slag and hinder the diffusion of oxygen. Especially, for high grade vanadium slags (V_2O_5 20-30%), such as South Africa vanadium slag or New Zealand vanadium slag (Huang, 2000), the hindrance becomes obvious due to the increase of corresponding sodium salts amount. So, diluting high-grade vanadium slag using reacted tailings is commonly conducted to improve conversion rate in vanadium-extraction plants.

Calcium salt roasting is an alternative to avoid the environmental problems (Peng et al., 2008; Zhang et al., 1993; Zhang and Wang, 2000). Instead of sodium salts, CaO is used as an additive during roasting process to produce calcium vanadates at relative higher temperature (850-950 °C), followed by leaching with sulfuric acid to obtain vanadate solutions. Through precipitation and calcination processes, the vanadium pentoxide are obtained (Li et al., 2016; Wen, 2009). The calcification roasting is considered as an environment-friendly method due to the elimination of pollutant gases. However, the harmful impurities, such as S, P, Cr and Fe, are also leached into the acidic solutions, bringing heavy burden for the subsequent product quality control. Based on the advantage of calcification roasting, Li (2016) proposed another method featured by calcification roasting-ammonium salt leaching. Ammonium carbonate replaced sulfuric acid to be used as leaching agent could greatly reduce the impurities amount in liquor. Li et al. (2017a; 2017b) proposed a new method, in which no salt was added during the roasting process. Calcification roasting and non-salt roasting are all cleaner processes and no toxic gases are produced during roasting. Ammonium metavanadate is directly formed by ammonium salt leaching. After crystallization, the mother liquor can be recycled for leaching, resulting in no high salinity ammonia containing wastewater formation. However, to treat high-grade vanadium slags, the recovery of vanadium is not satisfactory due to that some of V(VI) in clinker is no leachable in ammonium salt solutions.

Our previous work has proposed an all-hydrometallurgical process of extraction vanadium from vanadium slag. The vanadium spinel was strongly attacked by alkali medium and the trivalent vanadium is greatly oxidized by oxygen into pentavalent vanadium. This is an effective and cleaner process and the conversion of vanadium can attain above 90%, while alkaline medium can be recycled for leaching. Furthermore, this process can effectively extract any grade of vanadium slag. However, the high-alkali solutions of above 50 wt.% NaOH was used as leaching agent (Liu et al., 2013a; Liu et al., 2017; Pan et al., 2014; Wang et al., 2014). It means the evaporation energy consumption for the medium recycling is relatively high.

In view of the foregoing, we developed a new process of extraction vanadium by non-salt roasting, followed by low concentration alkaline leaching, which can effectively treat high-grade vanadium slag. Because the V(III) in vanadium slag is oxidized to V(V), which can be completely dissolved into alkaline solutions (Li et al., 2011a). The vanadium is finally extracted as sodium vanadate with a conversion of more than 90%. This new process has been proven to be environmental-friendly, and being able to avoid the generation of exhaust gases and wastewater. Moreover, the low concentration alkaline medium can be directly recycled for leaching without evaporation, which greatly decreases the energy consumption. This is an efficient extraction technology in term of energy and conversion consideration.

In this study, the decomposition mechanisms of vanadium slag in the roasting and leaching process was discussed. The effects of roasting temperature, roasting time, alkali concentration and leaching temperature on the recovery of vanadium were examined in detail.

2. Material and experimental

2.1 Materials

All the chemical reagents used were of analytical grade and deionized water was used throughout the experiments. The vanadium slag was supplied by Highveld Group Co. LTD, South Africa. Vanadium slag was first dried in oven at 80 °C for 2 h to remove moister, and then sieved to obtain particles of -200 meshes for further treatment.

2.2 Apparatus and procedure

Vanadium slag of - 200 meshes was roasted in muffle furnace (Fig. 1) for 3 h. During the roasting, the slag was stirred per 30 min to avoid agglomeration. After roasting, the roasted slag was air cooled to

room temperature and then milled and screened to obtain different particle size for leaching experiments.

Fig 1. The picture of muffle furnace (left) and pressure-resistant autoclave (right) used in experiment

The leaching experiments were performed in a 1.0 dm^3 pressure-resistant autoclave (Fig.1) with pressure range of 0-5 MPa (Gang et al., 2013). The reactor was loaded with vanadium slag, analytical grade NaOH, and predetermined amount of ultra-pure water. The mass ratio of alkali-to-ore was set to 5:1. Subsequently, the autoclave was sealed and stirred to keep the slurry suspended during the experiment. The autoclave was placed in the cavity of a heating furnace. Timing of the reaction was initiated when the autoclave was heated to the preset reaction temperature. At selected time intervals, about 10 g pulp was withdrawn quickly and separated by vacuum filtration to obtain residue for determining the vanadium extraction.

The conversion rate of vanadium was calculated using formula:

$$X = \left(\frac{M_V / M_{Ti} - m_V / m_{Ti}}{M_V / M_{Ti}} \right) \times 100\% \tag{1}$$

where M_V and m_V (unit: g) are the contents of vanadium metal in the original vanadium slag and in residue. M_{Ti} and m_{Ti} (unit: g) are the mass contents of Ti in the original vanadium slag and in residue, respectively.

Due to the undissolvable property of Ti during the ammonium salt leaching, Ti was used as the reference substance, and the mass content ratio change of vanadium to Ti was used as the evaluation parameter to calculate the conversion rate of vanadium.

2.3 Analysis instruments

The chemical and mineralogical analysis was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, PE Optima 7300DV, Perkin Elmer) and X-ray diffraction analysis (Phillips PW223/30), respectively. The scanning electron microscope- Energy Dispersive Spectrometer (SEM–EDS) images of the vanadium slag, clinker and the tailings were obtained by SEM (JSM-7001F + INCA, JEOL) with EDS equipment.

3. Results and discussion

3.1 Vanadium slag decomposition process

Table 1 shows the chemical composition of South Africa vanadium slag, indicating that vanadium, iron, silicon, and titanium are the main elements. Fig. 2 is the XRD pattern of the vanadium slag, clearly showing that the slag is mainly composed of vanadium spinel ((Mn,Fe)(V,Cr)$_2$O$_4$), esseneite (CaFeAlSiO$_6$) and titanic magnetite (Fe$_{2.5}$Ti$_{0.5}$O$_4$) phases. Fig. 3 is a back-scattered electron image of a vanadium slag particle, and three obvious phases can be observed. In order to identify the chemical composition of different phases, further examination of the element distribution of section 1, 2 and 3 in Fig. 3 using EDS has been performed and the analysis results were illustrated in Table 2. It is observed that the white phase (Section 3) mainly contains Mg, Al, Ti, V, Mn and Fe, which means the spinel co-exist as isomorphism with titanium magnetite. The gray one (Section 1) mainly contains Mg, Al, Si, Ca and Fe, which is identified to be esseneite, one of pyroxenes. The dark gray one (Section 2),

containing Na, Al, Si, Ca and Fe may be assigned to another complex pyroxene. It is clearly that vanadium spinel surrounded by pyroxene phases is the main vanadium-bearing phase in vanadium slag. In order to obtain a high conversion rate of vanadium, the structure of the pyroxene phases should be destroyed firstly to liberate the vanadium spinel and then it can contact and react with oxygen directly. The trivalent vanadium can be oxidized into tetravalent or pentavalent vanadium, which can be leached by alkaline solutions. Thus, the vanadium can be extracted by non-salt roasting-alkaline leaching method.

Table 1. Chemical analysis of the South Africa vanadium slag

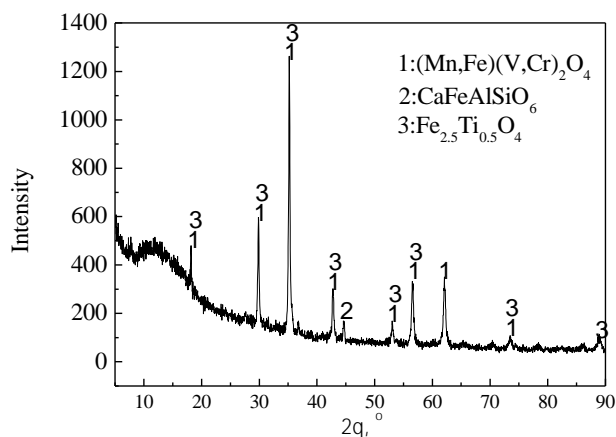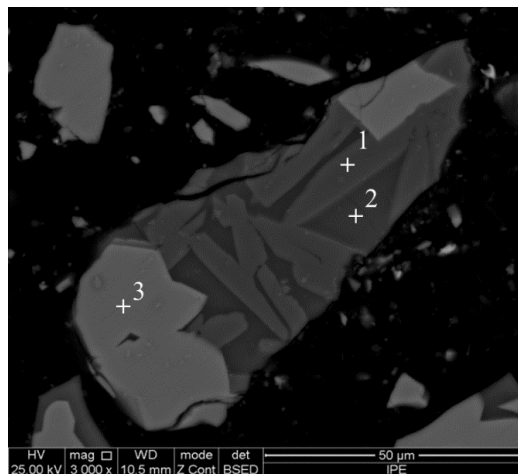| Component	V_2O_5	FeO	SiO_2	TiO_2	CaO	Cr_2O_3	MnO	Al_2O_3	MgO
Content, wt.%	21.23	35.6	12.82	10.92	2.01	3.39	3.76	5.18	3.28

Fig. 2. XRD pattern of the vanadium slag

Fig. 3. The back-scattered electron image of vanadium slag particle

Table 2. The element distribution of section 1, 2 and 3 in Fig. 3 by EDS (At., %)

No.	O	Na	Mg	Al	Si	Ca	Ti	V	Mn	Fe
1	35.09	0.49	3.37	5.84	22.45	15.26	4.76	0.33	1.63	10.79
2	36.38	8.67	—	8.25	26.43	6.34	0.7	—	2.37	10.86
3	22.4	—	3.03	2.63	—	—	12.18	19.92	7.38	27.82

3.2 Extraction of V under different reaction conditions

In order to establish the optimal reaction conditions for process development, critical parameters including roasting temperature, roasting time, alkali concentration and leaching temperature on the

recovery of vanadium were systematically studied with results being discussed in the following sections.

3.2.1 Effect of roasting temperature

The effects of roasting temperature ranging from 500 °C to 950 °C were examined as shown in Fig. 4 (A), while the other parameters were fixed with roasting time of 2 h, sodium hydroxide concentration of 30 wt.%, liquid-to-solid ratio of 5:1 and leaching temperature of 120 °C. It is obviously that the roasting temperature greatly affects the vanadium recovery. With the temperature increasing from 500 °C to 850 °C, the vanadium recovery dramatically increases from 25% to 93%. It indicates that the vanadium spinel was intensively decomposed within high temperature range. However, when the temperature is elevated to 950 °C, the vanadium recovery slightly decreases to 91%. The decline may be attributed to the warping of vanadium by low-molting-point reaction products, such as silicates. Hence, 850 °C was utilized in the following experiments.
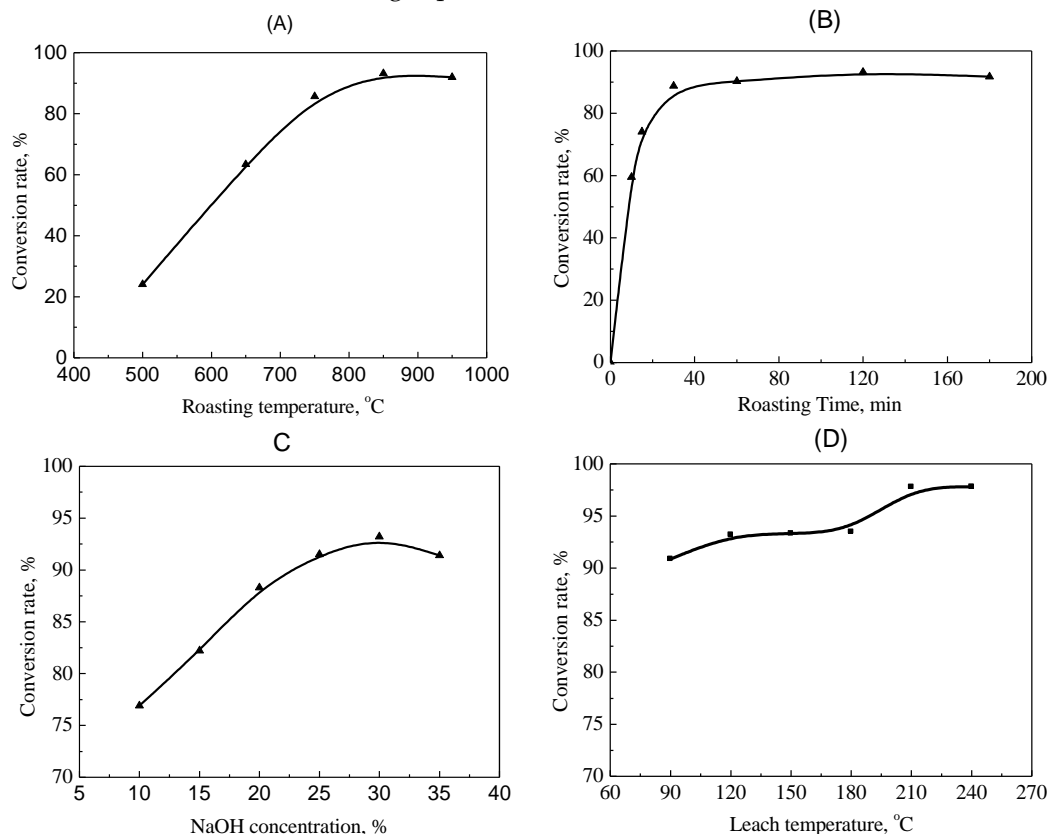

Fig. 4. The effect of roasting temperature (A), roasting time (B), NaOH concentration (C) and leaching temperature (D) on the extraction of vanadium

3.2.2 Effect of roasting time

The effect of roasting time on the vanadium recovery at 850 °C is illustrated in Fig. 4 (B). The leaching conditions are the same as above study. It can be seen that the recovery sharply increases to nearly 90% in 1.5 h. However, prolonging the roasting time, the vanadium recovery does not change significantly and even slightly decreases at 3 h. Long-time roasting at high temperature may lead to sintering, which greatly affects the vanadium extraction. Therefore, 2 h is selected as the optimal roasting time.

3.2.3 Effect of leaching alkali concentration

Fig. 4C illustrates the effect of alkali concentration on the vanadium extraction. When the alkali concentration increases from 10 wt.% to 30 wt.%, the conversion rate linearly increases from 76% to

92%. It means that the high alkalinity facilitates the decomposition of vanadium slag, especially for the silicate phases. The vanadium is ready to be dissociated from the Si-bearing warped phases and dissolved into the sodium hydroxide solutions. However, higher alkali concentration does not continuously increase the conversion rate. To reduce the consumption of alkali, 30 wt.% is chosen as the optimal alkali concentration.

3.2.4 Effect of leaching temperature

The influence of leaching temperature on the extraction of vanadium is illustrated in Fig. 4 (D), under the reaction conditions of roasting temperature of 850 ºC, roasting time of 2 h, alkali concentration of 30 wt.%, and liquid-to-solid ratio of 5:1. It is found that the roasted vanadium slag is easily leached out by NaOH solutions and the conversion rate can attain 91% at 90 ºC. Increasing the temperature to 120 ºC, the conversion rate is elevated to 93%. At 150 ºC and 180 ºC, the nearly same extraction is obtained. It seems that 120 ºC is the optimal leaching temperature. It is interesting to note that when the temperature is increased to above 210 ºC, the conversion rate can be furtherly elevated to 98%. It means the phases of tailings have changed at higher leaching temperatures, which allows the releasing and dissolving of wrapped vanadium. The decomposition mechanism will be discussed in detail in following sections. Higher extraction means the low production cost of vanadium pentoxide, therefore, 210 ºC is selected as the optimal leaching temperature.

As above discussed the optimal extraction conditions of vanadium from South Africa vanadium slag can be concluded as follows: roasting temperature of 850 ºC, roasting time of 2 h, leaching alkali concentration of 30 wt.%, leaching temperature of 210 ºC and leaching time of 2 h. Under these conditions, the conversion of vanadium can attain 98%. To well develop this new method, the roasting and leaching mechanisms should be deeply understood.

3.3 Reaction mechanisms

3.3.1 Roasting reaction mechanisms

Roasting is an extremely important process for the oxidation and extraction of vanadium. So, the decomposition behavior should be well understood. Fig. 5 illustrates the XRD pattern of roasted vanadium slag at different temperatures (roasting time 2h). At 500 ºC, the main new formed phases are magnetite (Fe_3O_4) and trans spinel (Fe_2VO_4). The weak diffraction peaks of hematite (Fe_2O_3) were simultaneously detected. It indicates that the Fe (II) was partially oxidized at low temperature. The Fe-
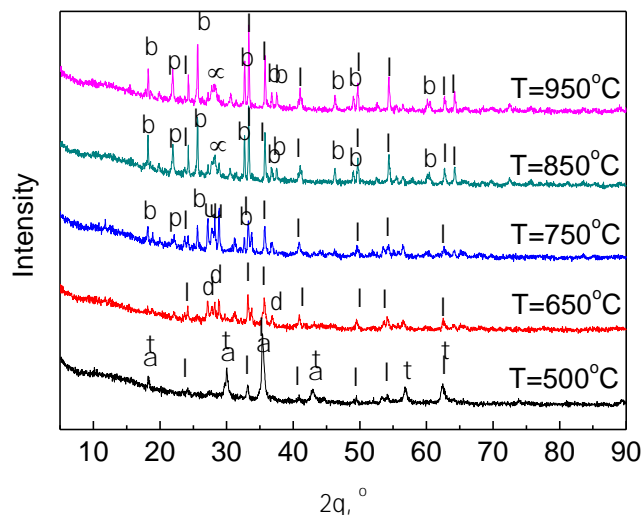

Fig. 5. The XRD pattern of roasted vanadium slag at various temperatures (τ-Fe_2VO_4, α-Fe_3O_4, β-Fe_2TiO_5, λ-Fe_2O_3, υ-V_2O_5, π-SiO_2, μ-$(Mg\,Mn)_2V_2O_7$, δ-VO_2)

containing phases, spinel and fayalite, transformed to trans spinel and magnetite respectively, and a small amount of latter was further oxidized to hematite. At 650 ºC, the characteristic diffraction peaks
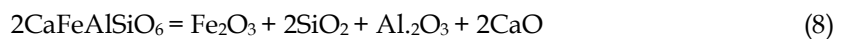
of magnetite disappeared and were totally replaced by hematite, which indicates Fe (II) was all oxidized to Fe (III). A new phase of vanadium dioxide also emerged at 650 ℃, which means that the V(III) began to be oxidized to V(IV)(ZHANG et al., 2015). When the temperature was elevated to 750 ℃, the new phases of vanadium pentoxide, quartz and pseudobrookite began to appear, which indicates the V(IV) was transferred to V(V) at 750 ℃ and the esseneite was decomposed. At 850 ℃ and 950 ℃, the same XRD diffractions were obtained as shown in Fig. 5. It is interesting to note that the formed vanadium pentoxide at low temperature (750 ℃) transformed to pyrovanadates of Mg and Mn (LI et al., 2017b; ZHANG et al., 2015). It corresponds to the optimal temperature of extraction vanadium, as shown in Fig. 4. Therefore, the pyrovanadates of Mg and Mn were considered as the final V-containing phases at 850 and 950 ℃.

Based on above discussion, the oxidation and decomposition behavior of vanadium slag during the roasting process can be understood. The possibly occurring reactions at different temperature stages are given as follows:

3. Partial oxidation of iron and vanadium (< 650 ℃):

$$2Fe + O_2 = 2FeO \tag{2}$$

$$6FeO + O_2 = 2Fe_3O_4 \tag{3}$$

$$FeV_2O_4 + Fe_3O_4 = 2Fe_2VO_4 \tag{4}$$

2. Further oxidation of iron and vanadium (650-750 ℃):

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \tag{5}$$

$$2Fe_2VO_4 + O_2 = 2Fe_2O_3 + 2VO_2 \tag{6}$$

$$4VO_2 + O_2 = 2V_2O_5 \tag{7}$$

$$2CaFeAlSiO_6 = Fe_2O_3 + 2SiO_2 + Al_2O_3 + 2CaO \tag{8}$$

3. Formation of pyrovanadates and pseudobrookite (750-900 ℃):

$$V_2O_5 + 2MnO = Mn_2V_2O_7 \tag{9}$$

$$V_2O_5 + 2MgO = Mg_2V_2O_7 \tag{10}$$

$$Fe_2O_3 + TiO_2 = Fe_2TiO_5. \tag{11}$$

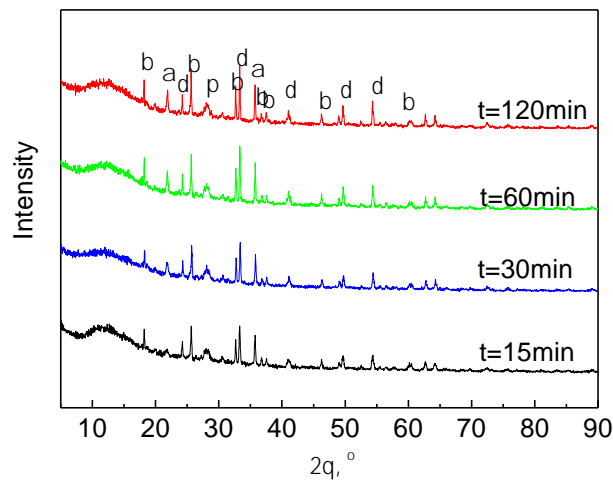This reaction progress was also confirmed by the other literatures (LI et al., 2017a; LI et al., 2017b).

Fig. 6. The XRD pattern of roasted vanadium slag at 850 ℃ (δ-Fe_2O_3, β-Fe_2TiO_5, π-$Mg_2V_2O_7$, α-SiO_2)

To well understand the reaction behavior, the phase change of vanadium slag at different time during the roasting process of 850℃ was investigated and the result is shown in Fig. 6. It was found that the origin phases were quickly decomposed within short time of 15 min, to form the new phases including of hematite, pseudobrookite, magnesium pyrovanadate and quartz. With increasing of roasting time, the roasted vanadium slag kept the totally same phase constitution. But the diffraction peaks became sharper, indicating the crystallinity of the new phases were becoming higher at high temperature.

Fig. 7 displays the cross-section of clinker particles and the corresponding element distribution of section 1, 2 and 3 is shown in Table 3. There are three distinct phases in the clinker. The light grey one (Section 1), vanadium dominated phase, mainly contains V, Mg, Mn and Si. As Fig. 5 suggested, it may correspond with the magnesium and manganese pyrovanadate. The dark grey one (Section 2) mainly contains Si, combined with Al, Na, Ca and V, which indicates that it may be a complex silicate. The white one (Section 3) mainly contains Ti and Fe, with a small amount of Mg and Al. It is certainly believed to be pseudobrookite. These phases are well consistent with the XRD analysis results.
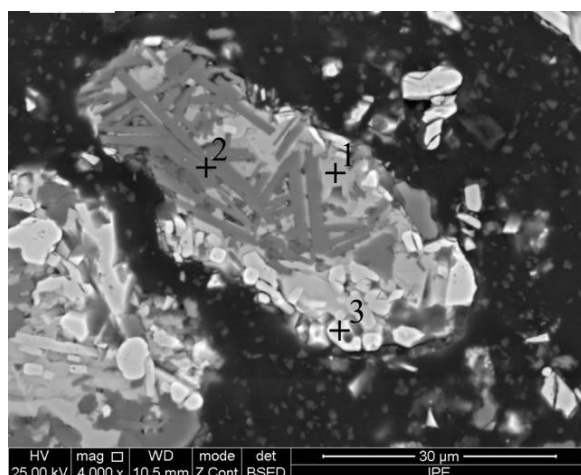

Fig. 7. The back-scattered electron image of roasted vanadium slag particle at 850 ^{o}C for 2 h.

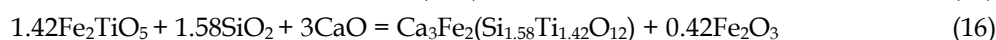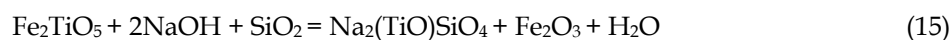Table 3. The element distribution of section 1, 2 and 3 in Fig. 7 by EDS (At., %)

No.	O	Na	Mg	Al	Si	Ca	Ti	V	Mn	Fe
1	67.77	—	9.43	—	2.50	1.62	0.19	12.17	5.38	0.91
2	63.02	4.92	—	9.79	19.16	1.96	—	1.16	—	—
3	74.86	—	2.48	4.26	—	—	1.43	0.43	0.59	13.05

3.3.2 Leaching reaction mechanisms

It is clear that the clinker is composed of hematite, pseudobrookite, pyrovanadate and quartz. Some phases can be decomposed in alkaline solutions and the XRD pattern of clinker after leaching was shown in Fig. 8. It is interesting to note that the phase composition of tailings at different leaching temperatures is not identical. At 120 ^{o}C and 150 ^{o}C, hematite and pseudobrookite constitute the main phases of tailings. Obviously, only pyrovanadates and quartz are decomposed and dissolved under this condition, and the reactions can be written as follows:

$$Mn_2V_2O_7 + 6NaOH = 2Na_3VO_4 + 2MnO + 3H_2O \tag{12}$$

$$Mg_2V_2O_7 + 6NaOH = 2Na_3VO_4 + 2MgO + 3H_2O \tag{13}$$

$$SiO_2 + 2NaOH = Na_2SiO_3 + H_2O \tag{14}$$

However, at a higher leaching temperature of 210 ^{o}C, the reaction phases have changed. The characteristic diffraction peaks of pseudobrookite disappeared and are replaced by calcium iron titanium silicate and natisite. It means except pyrovanadates and quartz, the pseudobrookite is also ready to be decomposed to natisite at higher leaching temperature. Meanwhile, the new silicate phase is formed under these conditions. The relevant reactions are as follows:

$$Fe_2TiO_5 + 2NaOH + SiO_2 = Na_2(TiO)SiO_4 + Fe_2O_3 + H_2O \tag{15}$$

$$1.42Fe_2TiO_5 + 1.58SiO_2 + 3CaO = Ca_3Fe_2(Si_{1.58}Ti_{1.42}O_{12}) + 0.42Fe_2O_3 \tag{16}$$

It is worth mentioning that a small amount of vanadium is wrapped in pseudobrookite as suggested by Table 3. The decomposition of pseudobrookite may result in the releasing of vanadium from vanadium slag particles. This convincingly explains why the conversion rate at 210 ^{o}C is higher than that at 120 ^{o}C (Fig. 4). So, 210 ^{o}C was selected as the optimal leaching temperature.
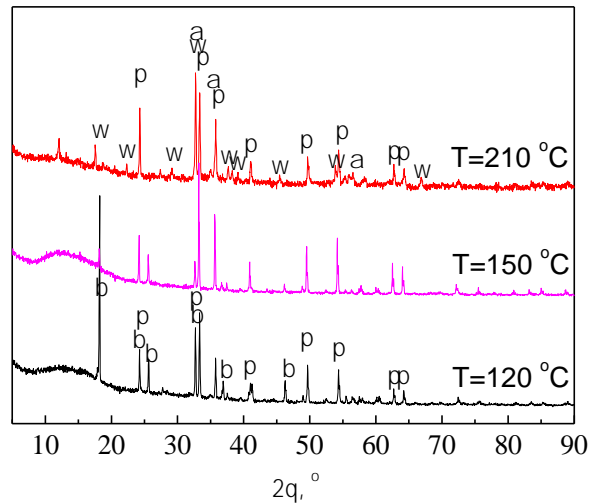
Fig. 8. The XRD pattern of leached vanadium slag at 120 °C, 150 °C and 210 °C (ω-Na$_2$(TiO)SiO$_4$, π-Fe$_2$O$_3$, α-Ca$_3$Fe$_2$(Si$_{1.58}$Ti$_{1.42}$O$_{12}$), β-Fe$_2$TiO$_5$).

Fig. 9 and Table 4 illustrate the back-scattered electron image of tailings and the corresponding element distribution. It is found that there is nearly no V-rich phase and the vanadium is almost entirely extracted at this temperature. Three phases can be distinguished by the grey degree. The Section 1 is dominated by iron. So, it is regarded as the hematite, containing some oxides of Mg, Al and Mn. The Section 2 mainly contains Ti, Fe and Na, being accompanied with Mg, Al, Si, Ca and Mn. It can be assigned to the mixed phases of calcium iron titanium silicate and natisite. The Section 3, containing Fe, Ti and Si, may be considered as mixed oxides.
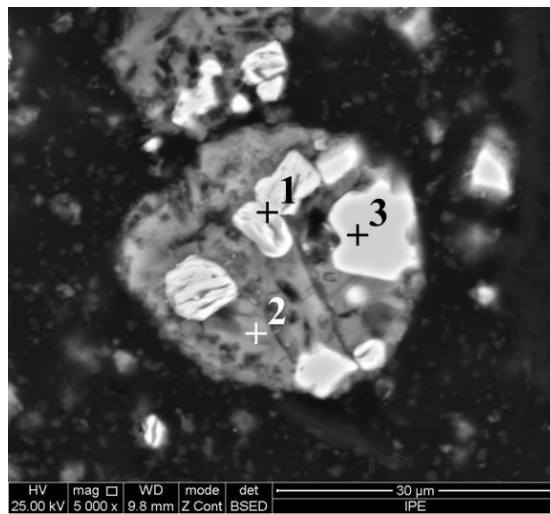

Fig. 9. The back-scattered electron image of tailings at 210 °C

Table 4. The element distribution of section 1, 2 and 3 in Fig. 9 by EDS (At., %)

No.	O	Na	Mg	Al	Si	Ca	Ti	V	Mn	Fe
1	34.01	—	1.73	3.51	—	—	3.63	0.43	1.88	48.18
2	40.35	1.94	1.29	1.12	3.91	4.36	14.61	0.5	2.29	25.9
3	68.53	—	—	—	6.49	—	8.06	—	—	16.92

4. Conclusions

This work proposed a new method of non-salt roasting-alkaline leaching to extract vanadium from vanadium slag. No roasting exhaust gases and wastewater are generated. It is an environmental-

friendly process and especially appropriate to treat high-grade vanadium slag. The reaction kinetic and mechanisms were discussed and the main conclusions are summarized as follows:

(1) Various parameters for the extraction of vanadium were investigated. The roasting temperature and leaching alkali concentration were confirmed to be two most significant factors on the vanadium extraction. Under the optimal conditions: roasting temperature of 850 ℃, roasting time of 2 h, alkali concentration of 30%, leaching temperature of 210 ℃ and leaching time of 2 h, the recovery of vanadium reached up to 98%. It indicates that this is an effective vanadium extraction method.

(2) XRD and SEM analysis indicates that the different phases of vanadium slag were decomposed at different temperatures. The iron-containing phases, silicate phases and spinel phases were oxidized in sequence when the temperature increased from 650 ℃ to 900 ℃. The pyrovanadates began to form at 900 ℃, which was believed to be the final V-containing phases and can be leached out by alkaline solutions.

(3) During the leaching process, the vanadium and silicon were leached into solutions to form sodium orthovanadate and sodium metasilicate. The recovery was above 90% within the temperature range of 90 ℃ to 240 ℃. It was interesting to note that when the temperature was increased from 180 ℃ to 210 ℃, the conversion rate was obviously elevated from 93% to 98%. It is owing to the fact that pseudobrookite was decomposed at high temperature to make the wrapped vanadium be released and leached into alkaline solutions.

References

BAROLIN, H., 1982. *Oxidation of vanadium slag*, Metallurgical Industry Press. Beijing, China.

CHEN, G., Wang, J., WANG, X., ZHENG, S., DU, H., ZHANG Y., 2013. *An investigation on the kinetics of chromium dissolution from Philippine chromite ore at high oxygen pressure in KOH sub-molten salt solution*, Hydrometallurgy. 139(3), 46-53.

GU, Y., ZHUANG, S., ZHONG, S., ZHOU, J., TIAN, J., HOU, M., 2007. *Non-pollution roasting technology to extracting vanadium from siliceous navajoite*, Chinese Journal of Rare Metals. 31(1), 102-106.

HUANG, D., 2000, Vanadium extraction & steelmaking, Metallurgical Industry Press. Beijing, China.

HUKKANEN, E., WALDEN, H., 1985. *The production of vanadium and steel from titanomagnetites*, International Journal of Mineral Processing. 15(1-2), 89-102.

LI, H., WANG, K., HUA, W., YANG, Z., ZHOU, W., XIE, B., 2016. *Selective leaching of vanadium in calcification-roasted vanadium slag by ammonium carbonate*, Hydrometallurgy. 160, 18-25.

LI, L., CHEN, D., BAI, R., ZHENG, S., DU, H., WANG, S., ZHANG, Y., 2011a. *Leaching of vanadium from vanadium-containing residue by NaOH sub-molten salt*, The Chinese Journal of Process Engineering. 11(5), 747-754.

LI, L., ZHANG, L., ZHENG, S., LOU, T., ZHANG, Y., CHEN, D., ZHANG, Y., 2011b. *Acid leaching of calcined vanadium titanomagnetite with calcium compounds for extraction of vanadium*, The Chinese Journal of Process Engineering. 11(4), 573-578.

LI, M., LIU, B., ZHENG, S., WANG, S., DU, H., DREISINGER, D. B., ZHANG, Y., 2017a. *A cleaner vanadium extraction method featuring non-salt roasting and ammonium bicarbonate leaching*, Journal of Cleaner Production. 149, 206-217.

LI, M., ZHENG, S., LIU, B., WANG, S., DREISINGER, D. B., ZHANG, Y., 2017b. *A clean and efficient method for recovery of vanadium from vanadium slag: nonsalt roasting and ammonium carbonate leaching processes*, Mineral Processing and Extractive Metallurgy Review. doi: http://dx.doi.org/10.1080/08827508.2017.1288117

LIAO, S., BO, T., 1985. *Vanadium metallurgy in foreign countries*, Metallurgical Industry Press. Beijing, China.

LIU, B., DU, H., WANG, S. N., ZHANG, Y., ZHENG, S. L., LI, L. J., CHEN, 2013a. *A novel method to extract vanadium and chromium from vanadium slag using molten NaOH-NaNO₃ binary system*, AIChE Journal. 59(2), 541–552.

LIU, H. B., DU, H., WANG, D. W., WANG, S. N., ZHENG, S. L., ZHANG, Y., 2013b. *Kinetics analysis of decomposition of vanadium slag by KOH sub-molten salt method*, Transactions of Nonferrous Metals Society of

China. 23(5), 1489-1500.

LIU, L., WANG, Z., DU, H., ZHENG, S., LASSI, U., ZHANG, Y., 2017. *Intensified decomposition of vanadium slag via aeration in concentrated NaOH solution*, International Journal of Mineral Processing. 160, 1-7.

MOSKALYK, R., ALFANTAZI, A., 2003. *Processing of vanadium: a review*, Minerals Engineering. 16(9), 793-805.

PAN, Z., ZHENG, S., WANG, Z., WANG, S., DU, H., ZHANG, Y., XIE, H., 2014. *Research on simultaneous extraction of vanadium and chromium from high chromium vanadium salg by sub-molten salt method*, Iron Steel Vanadium Titanium. 35(2), 1-8.

PENG, Y., ZHU, S., XIE, T., ZHANG, F., LIU, W., PAN, P., BIAN, W., 2008. China Patent No. CN101161831.

QIU, S., WEI, C., LI, M., ZHOU, X., LI, C., DENG, Z., 2011. *Dissolution kinetics of vanadium trioxide at high pressure in sodium hydroxide–oxygen systems*, Hydrometallurgy. 105(3), 350-354.

SHI, L., WANG, J., XIE, J., 2008. *Technology on vanadium extraction from bone coal by adding sodium chloride*, Mining and Metallurgical Engineering. 28(1), 58-61.

WANG, J., 2004, *Effect of calcium on leaching of vanadium from vanadium slag*, Sichuan Nonferrous Metals. 4, 27-29.

WANG, Z. H., ZHENG, S. L., WANG, S. N., LIU, B., WANG, D. W., DU, H., ZHANG, Y., 2014. *Research and prospect on extraction of vanadium from vanadium slag by liquid oxidation technologies*, Transactions of Nonferrous Metals Society of China. 24(5), 1273-1288.

WEN, L., 2009. *Process and development prospects of hydrometallurgical vanadium extraction from vanadium-bearing steel slag*, China Nonferrous Metallurgy. 3, 61-64.

ZHANG, J., ZHANG, W., ZHANG, L., GU, S., 2015. *Mechanism of vanadium slag roasting with calcium oxide*, International Journal of Mineral Processing. 138, 20-29.

ZHANG, P., JIANG, F., HE, Q., 1993. *The feasibility of extracting vanadium from low-grade vanadium ore by calcification roasting*, Iron Steel Vanadium Titanium. 14(2), 18-20.

ZHANG, Z., WANG, Y., 2000. *A new process of vanadium extraction from silica based vanadium ore by oxidation roasting with calcium compounds*, Chemical World, 41(6), 290-292.

ZHAO, T., 1999. *Nonferrous metal extractive metallurgy handbook*, Metallurgy Industry Publishing Company. Beijing, China