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Our journey in greenization of vanadium extraction from vanadium slag in China

Jie CHENG[1], Hong-yi LI[1,2], Dai-bo GAO[1], Xin-mian CHEN[1], Dong HAI[1], Jiang DIAO[1,2], Bing XIE[1], Fu-sheng PAN[1,2]

1. College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China;
2. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China

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Abstract: China is the world's largest producer of vanadium products, whose major vanadium resource is vanadium slag obtained by smelting vanadium−titanium magnetite ores. The vanadium extraction techniques from vanadium slag have progressed stepwise toward greenization during the past 30 years in China. This review has systematically summarized these developments and classified the developments into three stages. The early stage is the efficient vanadium extraction techniques such as the sodium roasting−water leaching technique. The developed stage is the clean vanadium extraction techniques including the calcification roasting−acid leaching technique and sub-molten salt technique. The advanced stage is the green vanadium extraction techniques, for example the magnesiation roasting−acid leaching technique. The mechanisms, advantages and disadvantages of industrially applied and literature reported vanadium extraction techniques in each development stage are elaborated from multiple perspectives. Finally, future development directions are pointed out, aiming to inspire green extraction technique of vanadium worldwide.

Key words: vanadium slag; vanadium; green extraction; roasting; leaching

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1 Introduction

Vanadium (V) element locates in the Group VB, Period 4 in the periodic table, with the electronic structure of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ and thus the multiple valences of V(II), V(III), V(IV), and V(V) [1,2]. Vanadium is praised as a modern industrial vitamin, widely used in metallurgical engineering, chemical engineering, energy storage, and aerospace [3−5]. Worldwide, about 92.9% of vanadium is used in steel-making with about 4% in nonferrous alloys and about 3% in the chemical industry, and batteries account for approximately 0.1% of vanadium consumption [6]. Vanadium distributes widely but extremely dispersedly in nature [7], whose resource forms include vanadium−titanium magnetite ores (VTMO), stone coals, petroleum, and bauxite [2,8−11]. Around the world, about 88% of vanadium is extracted from VTMO which are the major resource for vanadium extraction [12,13].

China has the largest vanadium resource reserves, accounting for 45.72% of the world's vanadium resource reserves [14,15]. Due to the lower vanadium concentration and more complex composition of VTMO in China, it is not easy to extract vanadium from these VTMO in China. Nevertheless, the vanadium extraction techniques have been innovated continuously to increase the vanadium extraction efficiency and simultaneously increase the cleanliness, which is to increase the greenization of vanadium extraction technique, in China.

In China, VTMO is smelted by blast furnace, during which vanadium is reduced into molten

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Corresponding author: Hong-yi LI, Tel: +86-23-65102469, Fax: +86-23-65127306, E-mail: hongyi.li@cqu.edu.cn

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iron [16]. The V-containing molten iron is blown by converter, during which vanadium is oxidized and enriched into the vanadium slag that is the raw material for subsequent vanadium extraction [17−19]. In the vanadium slag, the main form of V is FeV_2O_4 spinel [20]. Under the synergistic effect of oxygen and alkaline roasting additives, V(III) in the vanadium slag is oxidized into soluble vanadate (V(V)) during the roasting process [21]. Then, the soluble vanadate is transferred to the solution by leaching. After precipitation of vanadate and calcination of precipitate, the final product of V_2O_5 is recovered. In the entire process of extracting vanadium from vanadium−titanium magnetite ores, vanadium extraction from vanadium slag is the key step to determine vanadium recovery and environmental impact. Thus, the innovation of vanadium extraction technique mainly focuses on extracting vanadium from vanadium slag.

Although numerous techniques for extracting vanadium from vanadium slag have been reported, there is no review that can clearly show the greenization development of these techniques. In this work, the development and progress of vanadium extraction techniques are systematically reviewed from the traditional efficient extraction technique to the recent green extraction techniques. The aim is to provide insights and references for the design and development of green vanadium extraction techniques from vanadium slag.

2 Characteristics of vanadium slag

2.1 Chemical composition and phase component

The typical chemical compositions of vanadium slags produced by different plants are given in Table 1. Despite the chemical composition difference, the major phases of all vanadium slags are spinel and olivine phase, accompanied by the minor phase of pyroxene [6]. The V, Cr and Ti elements mainly exist as $(Fe,Mn)_2(V,Ti)O_4$ and $(Fe,Mg,Mn)(V,Cr)_2O_4$ spinels. The Si element exists in the major form of $(Fe,Mg)_2SiO_4$ olivine and the minor forms of $Ca(Fe,Mg)Si_2O_6$ and $Ca(Fe,Al)_2SiO_6$ pyroxenes.

2.2 Micromorphology and element distribution

Figure 1 shows the BSE image and the element linear scanning of vanadium slag. The distribution of Cr, V and Ti elements is consistent, and all of them are located in the bright regular region that corresponds to the spinel phase. The consistent distribution of Fe, Si and Mg in the areas surrounding spinels indicates that these areas are olivine phases. According to the linear scanning results, Cr spinel is located in the core region of the spinel particles, while V spinel is distributed in the outer layer with Ti spinel at the edge. This distribution characteristics is due to the crystallization ability and melting point increasing in order of Ti spinel < V spinel < Cr spinel [34].

3 Efficient techniques for vanadium extraction

In the preliminary development stage of vanadium extraction techniques, the researches focus on how to extract vanadium as efficiently as possible, emphasizing the improvement of vanadium recovery. In this development stage, the

Table 1 Typical chemical compositions of vanadium slags produced in different plants (wt.%)

Company	FeO	V_2O_3	Cr_2O_3	TiO_2	MnO	MgO	SiO_2	Ref.
Pan Steel	32.86−48.21	8.5−15.37	2.1−8.27	9.90−12.9	4.94−9.47	3.25−4.01	13.49−17.65	[13,22,23]
Chengde Steel	36.7−49.01	8.41−11.17	1.72−4.15	6.8−11.03	4.26−5.88	1.60	18.31−20.21	[24,25]
Weiyuan Steel	24.84	11.79	4.40	7.40	8.50	3.70	14.30	[26]
Jianlong Steel	23.50	11.31	9.19	10.45	6.73	1.17	14.62	[27]
Desheng Steel	31.78	17.15	10.58	8.52	6.16	0.89	8.48	[28]
Ma Steel	10−18	3.71	−	−	0.5−2.5	4−5	10−11	[6]
Esfahan Steel	15.76	1.62	−	0.98	4.52	0.89	6.88	[29]
British Steel	32	0.67	0.24	0.3	4.5	5.2	14	[30]
Swedish Steel	22.5	3.97	0.29	2.33	3.10	10	10.93	[31]
Isfahan Steel	9.42	1.01	−	1.45	4.19	4.22	13.7	[32]

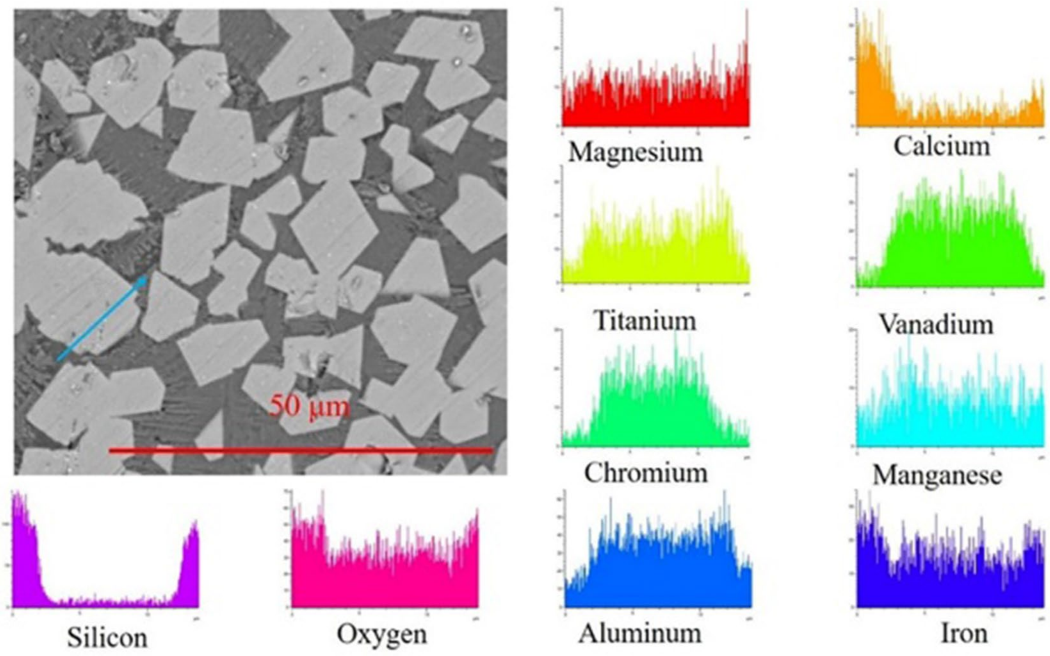

Fig. 1 BSE image and linear scanning results of vanadium slag (Adopted from LI et al [33])

environmental impact has been ignored.

3.1 Sodium roasting−water leaching

The sodium roasting−water leaching (SR−WL) technique for vanadium extraction was first proposed by BLEECKER in 1912 [2]. At present, this technique is the most widely used technique. Various sodium salts have been investigated as roasting additives at different temperature ranges ($NaOH-Na_2CO_3$: 600−1000 °C; $NaCl-Na_2SO_4-Na_2CO_3$: 800 °C) [12,35−37].

3.1.1 Monosodium roasting−water leaching

The commonly used alkaline additives in monosodium roasting include Na_2SO_4, NaCl, Na_2CO_3 and NaOH [38]. During the sodium roasting process, the olivine phase is converted into sodium silicates and Fe_2O_3 while the vanadium spinels are converted into water-soluble sodium vanadates. During the NaOH roasting process, major components in vanadium slag undergo chemical reactions Eq. (1) and Eqs. (S1)–(S3) in Supporting Information at 800 °C:

$$4FeV_2O_4+8NaOH+5O_2=8NaVO_3+2Fe_2O_3+4H_2O \quad (1)$$

During the Na_2SO_4 roasting process, chemical reactions below take place at 1200−1250 °C ((Eq. (2) and Eqs. (S4)−(S6) in Supporting Information):

$$4FeV_2O_4+4Na_2SO_4+3O_2=8NaVO_3+2Fe_2O_3+4SO_2 \quad (2)$$

For the Na_2CO_3 roasting process, chemical reactions ((Eq. (3) and Eqs. (S7)−(S9) in Supporting Information) take place at 800−1000 °C:

$$4FeV_2O_4+8NaCO_3+3O_2=8NaVO_3+2Fe_2O_3+8CO_2 \quad (3)$$

For the NaCl roasting process, chemical reactions ((Eq. (4) and Eqs. (S10)−(S12) in Supporting Information) below take place at 750−850 °C:

$$4FeV_2O_4+8NaCl+5O_2+4H_2O=8NaVO_3+2Fe_2O_3+8HCl \quad (4)$$

No matter which sodium salt is used as roasting additive, the major chemical principle of vanadium extraction is the same, which aims to convert V spinel (V(III)) in the vanadium slag into water-soluble sodium vanadates (V(V)) [15]. During water leaching, the sodium vanadates enter the solution and are thus separated from the leaching residues called vanadium extraction tailings [12]. The vanadium-containing solution is added with ammonium salts such as $(NH_4)_2SO_4$ to precipitate ammonium polyoxovanadates that are calcined to obtain the final product of V_2O_5. Due to the difference in reactivity and reaction kinetics of these sodium salts with V spinels, the resulted conversion rate of V in the similar roasting conditions descends in order of NaOH > Na_2SO_4 > Na_2CO_3 > NaCl [39].

3.1.2 Binary sodium salt roasting−water leaching

In order to improve the vanadium extraction efficiency and decrease the roasting temperature, binary sodium salt roasting is proposed: for example, the mixtures of $NaCl-Na_2SO_4$, $NaCl-Na_2CO_3$, $NaOH-Na_2CO_3$, and $NaCl-Na_2SO_4-Na_2CO_3$ as roasting additives for vanadium extraction. The chemical principles are similar to those of monosodium roasting−water leaching techniques. The highlight is that using sodium salt mixture with a low melting point can bring lower energy consumption and higher vanadium extraction efficiency for vanadium extraction.

3.2 Stepwise SR−WL

Whether using monosodium roasting or binary sodium roasting, the V and Cr elements in vanadium slag are converted synchronously and transferred together into the leaching solution in the subsequent leaching process. Then the V and Cr species were separated by solvent extraction [40] or ion exchange techniques [41]. V and Cr can be extracted simultaneously, which indicates the possible competition between V and Cr, leading to lower V extraction efficiency and the lower Cr extraction efficiency of only about 80% [37]. This not only requires larger extraction consumption, but also losses considerable amount of Cr resources.

To address this problem, based on the shell distribution characteristics of V and Cr in spinel particles of vanadium slag, LI et al [17] proposed the stepwise SR−WL technique to extract V and Cr separately (Fig. 2). At first, suitable one-step roasting and leaching conditions are selected to involve vanadium spinel participating in the reaction, while chromium spinel hardly participates in the reaction. The vanadium and chromium extraction efficiencies are 88.6% and 7.0%, respectively. After one-step process, the leaching residue obtained is roasted and leached under the

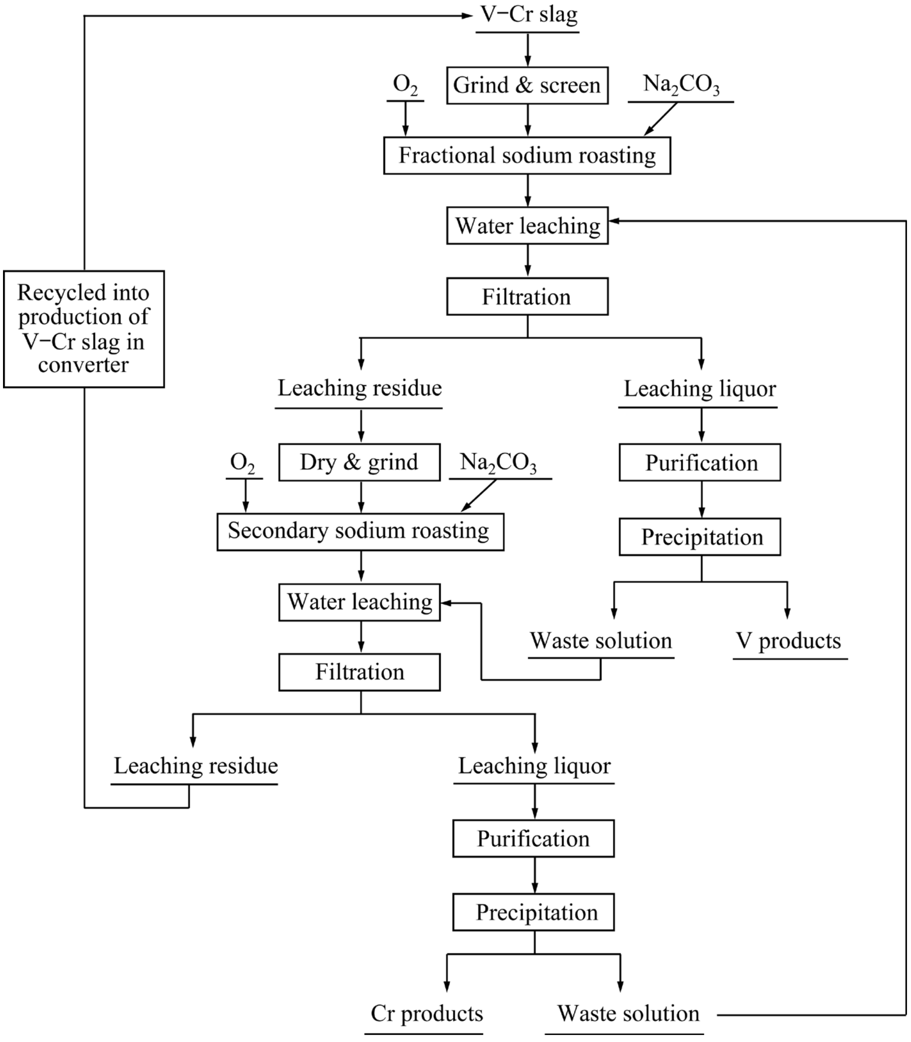

Fig. 2 Flowchart of stepwise SR−WL process (Adopted from LI et al [17])

optimal conditions. The vanadium extraction efficiency is 90.67% and the chromium extraction efficiency is 95.36%. During the entire process, the comprehensive vanadium and chromium extraction efficiencies can reach 99.0% and 95.7%, respectively.

3.3 Sodium roasting−$(NH_4)_2SO_4$ leaching

Although ammonium salt vanadium precipitation is a very mature vanadium precipitation process, it still generates a series of vanadium precipitation wastewater during the vanadium precipitation process, causing environmental pollution. In order to reduce this harm, WEN et al [35] proposed to use ammonium salt solution instead of water in the leaching process, so that vanadium precipitation wastewater could be recycled as the leaching medium. The vanadium and chromium extraction efficiencies can reach 94.6% and 96.5%, respectively. $(NH_4)_2SO_4$ in the leaching solution does not play a significant role in the leaching process, as sodium vanadate and sodium chromate are water-soluble. The role of $(NH_4)_2SO_4$ lies in the process of vanadium precipitation by ammonium salt after leaching. 94.8% vanadium can be precipitated in the form of ammonium polyvanadate. Afterwards, $Na_2S_2O_5$ is added to the supernatant after vanadium precipitation for reducing chromium. The chromium precipitates in the form of chromium hydroxide. Then, ammonium polyvanadate and chromium hydroxide are calcined separately to obtain V_2O_5 (purity: 91.49%) and Cr_2O_3 (purity: 89.89%).

However, the essence of this technique still utilizes the principle of traditional SR−WL technique. Thus, although the discharge of ammonia nitrogen wastewater has been reduced, most problems in the process of roasting−leaching have not been improved.

3.4 Method summary and evaluation

The SR−WL technique is the most developed vanadium extraction technique, which is widely applied in the vanadium extraction industry in China. Although various leaching methods can be coupled to the sodium roasting process, this category of vanadium extraction techniques suffer from problems below:

(1) Emission of toxic gases such as Cl_2, HCl, SO_2 and SO_3 causes serious air pollution and corrodes equipment [42].

(2) Discharge of concentrated ammonia nitrogen wastewater (generating over 2×10^6 t per year) [43,44]. After V precipitation, high concentration of Na^+ ions are left in the wastewater. After the recycling of water resource in the resulted wastewater, a large amount of $Na_2SO_4/(NH_4)_2SO_4$ complex salt mixture is generated, which is unusable and discarded as solid wastes.

(3) 7−8 t of solid wastes, including the vanadium extraction tailings, are generated for each 1 t of V_2O_5 product [13]. Due to the high Na content, the tailings cannot be recycled to the metallurgical process of vanadium slag production for waste digestion and further resource extraction.

Apparently, the sodium roasting techniques have low greenization level. These problems above are all caused by the introduction of sodium salts during the roasting process. Na facilitates the V conversion and extraction, after which it needs an issue to exclude itself from the V extraction product line, resulting in the large amount of Na-bearing wastes. Therefore, to settle the problem of large-scale discharge of solid waste, it is necessary to optimize roasting additives.

4 Clean techniques for vanadium extraction

The “clean vanadium extraction” refers to both high vanadium extraction efficiency and high overall resource utilization of vanadium slag, while also ensuring that the vanadium extraction process minimizes environmental pollution. Based on the in-depth study of the hazards of SR−WL, the researchers found that to solve the problem, it is necessary to replace the roasting additives. Thus, they proposed calcification roasting.

4.1 Calcification roasting−acid leaching

Calcification roasting was proposed by the Tula factory in Russia as early as the 1970s [45]. Due to the lower extraction efficiency of vanadium compared to sodium roasting, it was not initially used in industrial application. However, the vanadium extraction process using this technique not only has low additive costs but also does not emit polluting gases, which has attracted more and more attention from researchers [46−48]. At present, the first production line of calcification roasting−acid leaching (CR−AL) of vanadium slag was established by Panzhihua Steel in Xichang, China in 2012, with the production of 18000 t V_2O_5 per year.

4.1.1 Calcification roasting−sulfuric acid leaching

In the calcification roasting process, $CaCO_3$/CaO is used as the roasting additive to oxidize V(III) in vanadium slag to calcium vanadate (V(V)) under the synergistic action of oxygen [45]. Calcium vanadate is soluble in acid [48−50]. Therefore, calcium vanadate is transferred into the solution by sulfuric acid leaching and separated from vanadium extraction tailings. Ca^{2+} reacts with SO_4^{2-} to form $CaSO_4$ precipitation and enters the vanadium extraction tailings [51]. The vanadium-containing solution is subjected to ammonium salt precipitation (precipitation calcination) to obtain the V_2O_5 product. The main reactions ((Eqs. (5)−(7) and Eqs. (S13)−(S14) in Supporting Information) that occur during roasting process are as follows:

$$4FeV_2O_4+4CaO+5O_2=4CaV_2O_6+2Fe_2O_3 \quad (5)$$

$$4FeV_2O_4+8CaO+5O_2=4Ca_2V_2O_7+2Fe_2O_3 \quad (6)$$

$$4FeV_2O_4+12CaO+5O_2=4Ca_3V_2O_8+2Fe_2O_3 \quad (7)$$

The main reactions of leaching process are

$$CaV_2O_6+2H_2SO_4=(VO_2)_2SO_4+CaSO_4+2H_2O \quad (8)$$

$$Ca_2V_2O_7+3H_2SO_4=(VO_2)_2SO_4+2CaSO_4+3H_2O \quad (9)$$

$$Ca_3V_2O_8+4H_2SO_4=(VO_2)_2SO_4+3CaSO_4+4H_2O \quad (10)$$

$$CaCrO_4+H_2SO_4=H_2CrO_4+CaSO_4 \quad (11)$$

Compared with SR−WL, calcification roasting−sulfuric acid leaching emits non-toxic and harmless gases. During the evaporation and recovery of water resources from wastewater, no refractory calcium salt solid waste is generated, and only ammonium sulfate which can be recycled in the precipitation is formed. Compared with SR−WL technique, calcification roasting−sulfuric acid leaching is a clean technique. However, due to the uniform mixing of $CaSO_4$ precipitates into vanadium extraction tailings, high S content leads to the failure of recycling of this vanadium extraction tailings to recover iron and manganese resources.

4.1.2 Calcification roasting−($(NH_4)_2SO_4$−H_2SO_4) leaching

Influenced by the idea of sodium roasting−$(NH_4)_2SO_4$ leaching technique, WEN et al [52] proposed the calcification roasting−($(NH_4)_2SO_4$−H_2SO_4) synergistic system leaching. The flowchart of the whole process is shown in Fig. 3. The vanadium extraction efficiency is 93.45%, while the chromium extraction efficiency is only 0.24%. Then, the leaching solution pH is adjusted to be 8.0 and the solution is heated at 60 °C for 60 min. 99.75% vanadium is precipitated in the form of $(NH_4)_2V_6O_{16}$ and V_2O_5 (purity: 95.71%) is obtained after calcination. Compared with the calcification roasting−sulfuric acid leaching, the vanadium extraction efficiency is higher and the chromium extraction efficiency is lower. This is due to the addition of $(NH_4)_2SO_4$ promoting the acid leaching reaction and improving the vanadium extraction efficiency. In addition, the optimal leaching temperature (20 °C) used in this technique is lower than the leaching temperature (70 °C) of calcification roasting−sulfuric acid leaching, resulting in low economic cost. The leaching process does not require real-time pH monitoring and is easy to control. The recycling of NH_4^+ effectively reduces the content of ammonia nitrogen wastewater. However, this technique still has similar issues as calcification roasting−sulfuric acid leaching.

4.1.3 Microwave calcification roasting−sulfuric acid leaching

Recently, microwave roasting technique has been widely used in metal extraction due to its advantages such as high thermal efficiency, rapid heat transfer, and ease of automation and process control [53]. The main features of microwave radiation applications in metallurgy are the potential for microwave roasting to facilitate new forms of metal extraction in a controlled environment and enhance mineral surface chemistry [54].

Based on this, GAO et al [55] proposed the use of microwave roasting technique to extract vanadium. The vanadium extraction efficiency can reach 98.29% and the chromium extraction efficiency is 4.32%. Compared to conventional muffle furnace roasting, microwave heating operates from the inside out. Due to differences in dielectric constant and heat capacity, different phases have different heat propagation velocities and temperatures, resulting in larger temperature gradients. This results in a large temperature difference between inside and outside the sample, which induces cracks at the ore phase boundary and is more conducive to the oxidation of the sample. Therefore, this technique can reduce the roasting temperature, accelerate the oxidation and

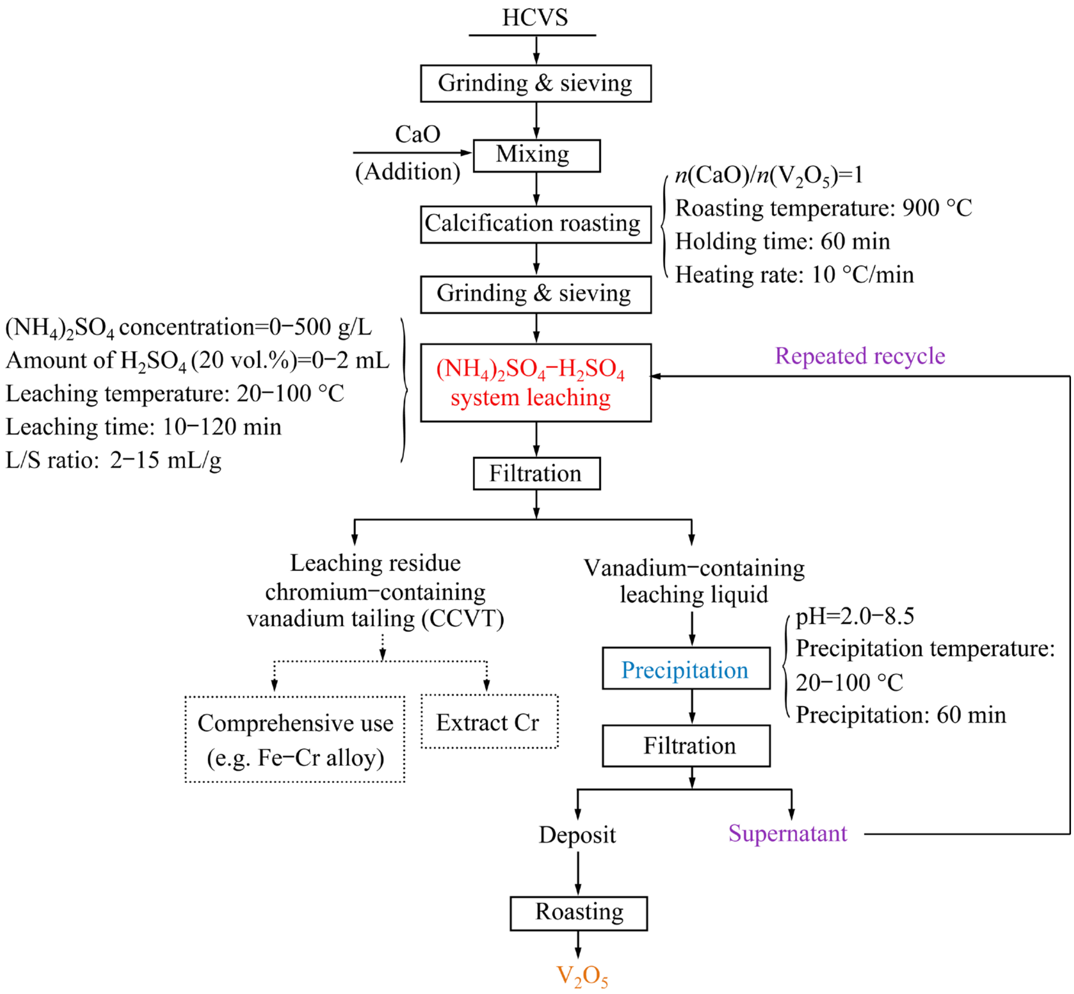

Fig. 3 Flowchart of calcification roasting−($(NH_4)_2SO_4$−H_2SO_4) leaching (Adopted from WEN et al [52])

decomposition of minerals, and shorten the holding time. However, $CaSO_4$ is still produced in the leaching process, and the leaching time and temperature used in this technique are higher than those used in conventional muffle furnace roasting, which greatly increases the economic cost to a large extent.

4.2 Calcification roasting−ammonium carbonate leaching

Due to the generation of $CaSO_4$ during the CR−AL process, the amount of solid waste increases. In the calcification roasting process, phosphorus is converted into tricalcium phosphate. Then, tricalcium phosphate reacts with sulfuric acid to form phosphate ions into vanadate-containing leaching solution and combines with vanadate ions to form heteropoly acid anion in the leaching process, which inhibits the precipitation of ammonium vanadate and thus reduces the vanadium extraction efficiency [56]. So, LI et al [21] proposed a new leaching technique for ammonium carbonate based on the differences in reactivity (calcium vanadate can react with ammonium carbonate, while calcium phosphate cannot react with ammonium carbonate). The flowchart is shown in Fig. 4. The vanadium extraction efficiency can reach 96%, while the phosphate extraction efficiency is only 9.2%. Vanadium can be precipitated directly after cooling in the form of ammonium vanadate. And the vanadium precipitation wastewater can be used for cyclic leaching. With this technique, vanadium can be selectively introduced into the leaching solution, while phosphorus remains in the leaching residue. Compared with traditional acid leaching, the impurity content of vanadium leaching solution obtained by this technique is lower. This not only improves the vanadium extraction efficiency, but also increases economic benefits. But the amount of

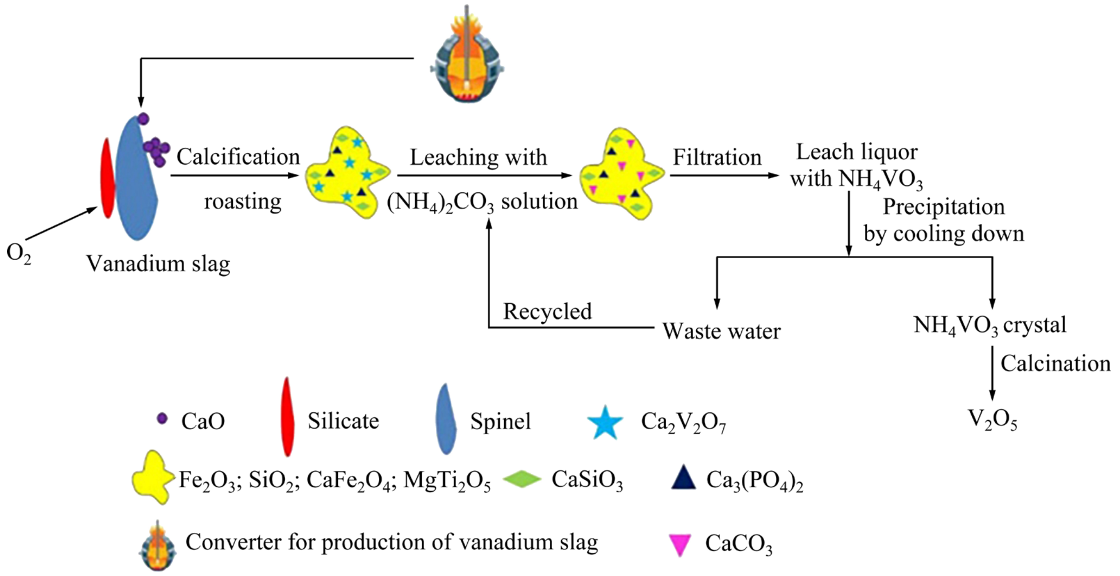

Fig. 4 Flowchart of calcification roasting−ammonium carbonate leaching (Adopted from LI et al [21])

leaching agent used in this technique is larger than that of other leaching technique. Although its vanadium precipitation wastewater can be recycled, the scale of wastewater generated is still relatively large.

4.3 Calcification roasting−sodium carbonate leaching

Due to the presence of a few chromium in the vanadium-containing wastewater during the calcification−roasting−acid leaching process, the concentration of chromium is much higher than the national vanadium pollutant emission standard. Therefore, WEN et al [57] proposed a more thorough vanadium chromium separation technique based on the calcification roasting process, which uses sodium carbonate as a leaching agent for vanadium extraction. The flowchart is shown in Fig. 5. The reactions occur during the leaching process as follows:

$$CaV_2O_6+Na_2CO_3=CaCO_3\downarrow+2NaVO_3 \qquad (12)$$

$$Ca_2V_2O_7+2Na_2CO_3=2CaCO_3\downarrow+Na_4V_2O_7 \qquad (13)$$

$$Ca_3V_2O_8+3Na_2CO_3=3CaCO_3\downarrow+2Na_3VO_4 \qquad (14)$$

The vanadium extraction efficiency is 93.19%, while the chromium extraction efficiency is only 0.04%.

4.4 Sub-molten salt technique

In view of the problems existing in the traditional processes of sodium roasting and calcification roasting, LIU et al [58] proposed and developed the sub-molten salt vanadium extraction technique. This technique has been established on industrial demonstration production line in 2017 in Chengde Iron and Steel Group, China. The sub-molten salt vanadium extraction technique has the characteristics of clean and efficient, which is an important research direction for vanadium extraction. Sub-molten salt is a special melt containing a little water. It is usually a high concentration aqueous solution of alkali metal salts, and belongs to a new type of reaction medium. The sub-molten salt vanadium extraction technique is a liquid-phase oxidation decomposition process of vanadium slag using 30%−80% NaOH or KOH solution or $NaNO_3$−NaOH binary molten-salt as the medium, through a pseudo homogeneous reaction at 200−400 °C [59]. Compared with the traditional vanadium extraction technique (roasting−leaching), the solid waste production rate of sub-molten salt extraction technique is significantly reduced, which belongs to the clean vanadium extraction technique.

4.4.1 Monobasic sub-molten salt

(1) NaOH sub-molten salt

The main phases of vanadium slag Fe_2SiO_4, FeV_2O_4 and $FeCr_2O_4$ have the following oxidation decomposition reactions ((Eq. (15) and Eqs. (S15)–(S17) in Supporting Information) in the medium of NaOH sub-molten salt:

$$4FeV_2O_4+24NaOH+5O_2= \\ 2Fe_2O_3+12H_2O+8Na_3VO_4 \qquad (15)$$

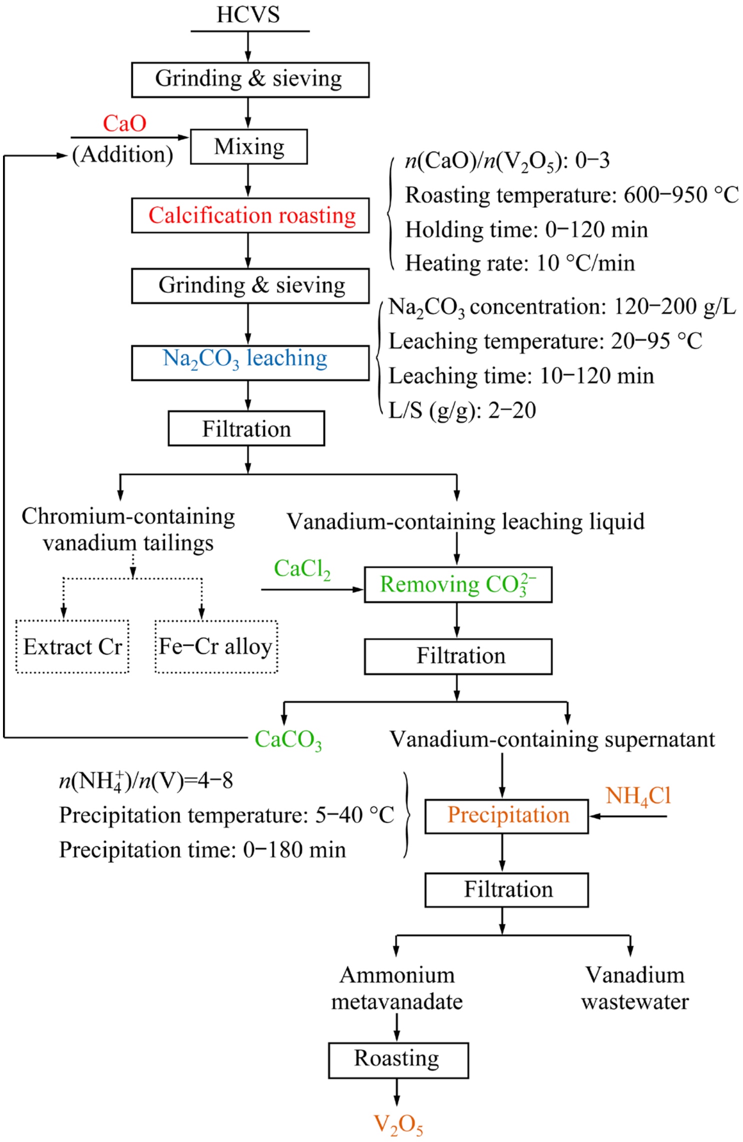

Fig. 5 Flowchart of calcification roasting−sodium carbonate leaching (Adopted from WEN et al [57])

The molten salt contains highly chemically active reactive oxygen species. With leaching time of 180 min, L/S ratio of 6:1 (mL/g), NaOH mass concentration of 50%, stirring speed of 700 r/min, oxygen pressure of 1MPa at 200 °C, the vanadium and chromium extraction efficiencies of 98.3% and 93.3% were obtained [28]. The vanadium and chromium are separated and the vanadium-containing solution is crystallized to obtain Na_3VO_4 products.

(2) KOH sub-molten salt

The principle of extracting vanadium with KOH sub-molten salt is similar to that of vanadium slag with NaOH sub-molten salt. The main chemical reactions ((Eq. (16) and Eqs. (S18)–(S20) in Supporting Information) occur as follows:

$$4FeV_2O_4+24KOH+5O_2= \\ 2Fe_2O_3+12H_2O+8K_3VO_4 \qquad (16)$$

Under the optimal reaction conditions (reaction time: 5 h, temperature: 180 °C, oxygen flow rate: 1 L/min, L/S ratio: 4:1 (mL/g) and stirring speed: 700 r/min), the vanadium and chromium extraction efficiencies are 95% and 90%, respectively [42]. The vanadium and chromium are separated and the vanadium solution is crystallized to obtain K_3VO_4 products.

4.4.2 Binary sub-molten salt

Due to the strong oxidation and high-temperature instability of $NaNO_3$, the addition of $NaNO_3$ to NaOH sub-molten salt can be oxidized directly or through decomposition to produce O_2 indirect oxidation of V(III) and Fe(II) in vanadium slag [25]. The chemical reactions involved ((Eq. (17) and Eqs. (S21)−(S23) in Supporting Information) in the $NaNO_3$−NaOH binary sub-molten salt system are as follows:

$$2FeV_2O_4+12NaOH+5NaNO_3= Fe_2O_3+6H_2O+4Na_3VO_4+5NaNO_2 \quad (17)$$

NaOH provides a medium for the reaction, which is conducive to the decomposition of acidic oxides. NaOH enhances the decomposition reaction of $NaNO_3$, while producing reactive oxygen species (O and O^{2-}). In addition, the addition of $NaNO_3$ reduces the amount of NaOH, ensuring complete oxidation and conversion of vanadium spinel into Na_3VO_4 while reducing the formation of Na_2SiO_3. From the aspect of kinetics, it is conducive to the subsequent leaching of Na_3VO_4. However, in order to fully decompose and utilize $NaNO_3$, it is necessary to increase the vanadium extraction temperature to above 375 °C. The reaction time is increased to 2−3 times the time required for decomposition of vanadium slag. This significantly increases the energy consumption of vanadium extraction process.

4.5 Method summary and evaluation

CR−AL technique and the sub-melt salt technique have been used in industry. However, the CR−AL is similar to the common SR−WL technique in that it requires alkaline roasting additives to convert V(III) in vanadium slag to soluble vanadates (V(V)). Vanadates are leached into the solution phase, followed by vanadium precipitation and calcination to recover vanadium oxides. Alkaline additives fulfill their mission after forming soluble vanadates, which eventually leads to the formation of wastewater and solid waste that are difficult to treat. The existing vanadium extraction technique can extract more than 79% of vanadium (industrial vanadium extraction efficiency is 79%−81%, laboratory vanadium extraction efficiency can reach over 90%), while valuable resources such as Fe and Mn remain in vanadium extraction tailings. The alkaline metals in the roasting additives also remain in the vanadium extraction tailings after completing its mission. The alkaline metals (such as Na) or elements introduced by their symbiosis (such as S) are corrosive and difficult to separate from the linings of blast furnaces and converter furnaces [60]. This makes it difficult to utilize the vanadium extraction tailings, and valuable resources such as Fe and Mn in the tailings are abandoned. This has caused serious resource waste, resulting in a low resource utilization rate in the entire vanadium slag extraction process.

The sub-molten salt vanadium extraction technique established to address this issue does not generate waste gas or wastewater during the decomposition of vanadium slag, which is a green production step. However, in order to obtain widely used and market recognized V_2O_5 products, this technique needs to implement deep processing of vanadates. The deep processing steps such as electrolysis generate wastewater that is difficult to treat and utilize, increasing energy consumption. Meanwhile, a small amount of chromate is mixed in the obtained vanadates, which needs to be purified by solvent extraction and other methods before further processing. Only in this way can V_2O_5 products that meet the purity requirements be prepared. These purification and deep processing steps inevitably produce wastewater and solid waste. In addition, calcium silicate is formed when adding Ca to the alkaline solution to remove Si. In vanadium slag, due to the silicon (SiO_2) content of about 20%, about half of which enters the alkaline solution, numerous calcium silicate solid waste is generated. The Fe_2O_3 content in the vanadium extraction tailings is about 50%. However, due to high Na content, it cannot be extensively recycled to the pre-metallurgical process for Fe recovery. This not only generates a mass of solid waste, but also causes waste of Fe resources. It is reported that the sub-molten salt technique generates 1 t of solid waste for per 1 t of V_2O_5.

5 Green techniques for vanadium extraction

From efficient vanadium extraction techniques to clean vanadium extraction techniques, the cleanliness and environmental friendliness of the vanadium extraction process are constantly improved. However, the problems of large solid waste emissions and low resource utilization have not been completely resolved. The fundamental reason is that the alkaline metal elements in the additives remain in the vanadium extraction tailings and are difficult to selectively separate. Based on this, researchers have developed a new concept of "green vanadium extraction" through continuous exploration and research. Green vanadium extraction from vanadium slag contains two meanings: (1) "Clean", which means that the emissions of "three wastes" are small and the process is environmentally friendly; (2) "Efficient", which requires both high vanadium extraction efficiency of vanadium slag and high overall resource utilization rate of vanadium slag, making full use of various resources in vanadium slag as much as possible. To achieve this goal, it is necessary to revolutionarily develop new techniques for green vanadium extraction from vanadium slag.

5.1 Magnesiation roasting−acid leaching

Driven by the concept of green vanadium extraction, LI et al [13] proposed a new technique of vanadium extraction by magnesiation roasting−acid leaching based on magnesium cycle. Through the recycling of MgO, the whole components of vanadium extraction wastewater can be recycled in vanadium extraction system and the full quantitative recycling of vanadium extraction solid waste. Thus, zero emission of "three wastes" can be achieved and the resource utilization rate of vanadium slag can be significantly improved. The flowchart is shown in Fig. 6. The main reactions ((Eqs. (18−20) and Eq. (S24) in Supporting Information) that occur in the roasting process are as follows:

$$4MgO+4FeV_2O_4+5O_2=4MgV_2O_6+2Fe_2O_3 \tag{18}$$

$$8MgO+4FeV_2O_4+5O_2=4Mg_2V_2O_7+2Fe_2O_3 \tag{19}$$

$$12MgO+4FeV_2O_4+5O_2=4Mg_3V_2O_8+2Fe_2O_3 \tag{20}$$

Then, the roasted sample is leached with sulfuric acid solution with pH of 0.5. Under the acidic conditions, magnesium vanadate is converted to $(VO_2)_2SO_4$ into the acid leaching solution. The vanadium extraction efficiency can reach 95.56%. Vanadium-containing leaching solution is precipitated with ammonium sulfate to obtain ammonium polyvanadate precipitates, which is then calcined to obtain V_2O_5 product (purity >99%). The ammonia gas generated by the decomposition process is collected for subsequent recovery of manganese and magnesium.

Due to the fact that almost all of the initially added MgO has been transferred to the solution through roasting and acid leaching steps, magnesium can be recovered and recycled in a full amount. The residual solution is mainly ammonium sulfate solution, which is crystallized to recover ammonium sulfate crystal. 90% ammonium sulfate

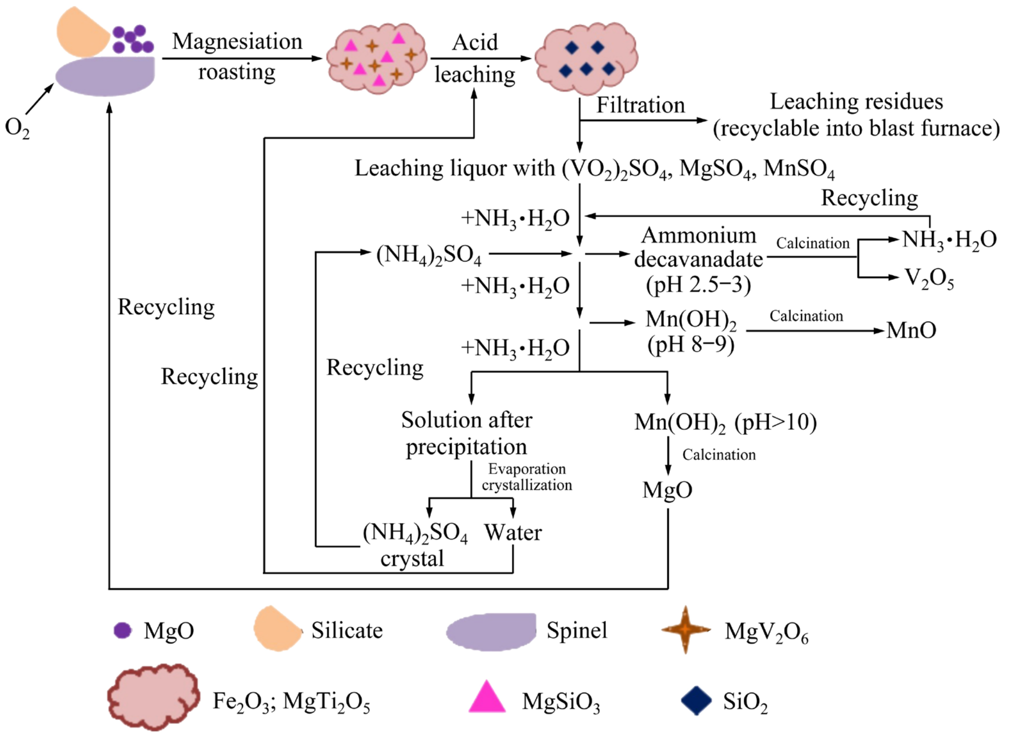

Fig. 6 Flowchart of magnesiation roasting−acid leaching (Adopted from LI et al [13])

is recycled for the acid ammonium salt vanadium precipitation step, and 10% is used as a byproduct of ammonium sulfate. The residual water is recycled as diluent for the leaching step. Vanadium extraction tailings mainly contain Fe_2O_3 and SiO_2. Therefore, it can be returned to the blast furnace to recover iron resources and residual vanadium in vanadium extraction tailings.

5.2 Manganese roasting−acid leaching

The vanadium slag itself contains alkaline manganese (MnO <10%) and mainly in the form of manganese spinel. In view of this, JIANG et al [60,61] proposed a technique for extracting vanadium by manganese roasting−acid leaching. With $MnCO_3/MnO_2$ as roasting additive, manganese roasting of vanadium slag is carried out, and the process is shown in Fig. 7. The main reactions ((Eq. (21) and Eq. (S25) in Supporting Information) that occur in the roasting process are as follows:

$$2FeV_2O_4+4MnCO_3+2.5O_2= \\ Fe_2O_3+2Mn_2V_2O_7+4CO_2 \quad (21)$$

Then, the roasted sample is leached with sulfuric acid solution (pH=2.5). The vanadium extraction efficiency is 89%. Vanadium-containing leaching solution is precipitated with ammonium sulfate to obtain ammonium polyvanadate precipitation, which is then calcined to obtain V_2O_5 product (purity >99%).

5.3 Method summary and evaluation

The magnesiation roasting−acid leaching and manganese roasting−acid leaching techniques have greatly improved their cleanliness and resource utilization compared to the above-mentioned vanadium extraction technique due to the use of selective separation, recovery, and recycling roasting additives. The specific advantages are as follows:

(1) Zero emission of “three wastes” has been achieved. No exhaust gas is produced during the vanadium extraction process. All major components of vanadium extraction wastewater are separated and recovered, and recycled in vanadium extraction system. Due to its friendly composition with the blast furnace lining, the vanadium extraction tailings can be completely returned to the blast furnace for resource recycling.

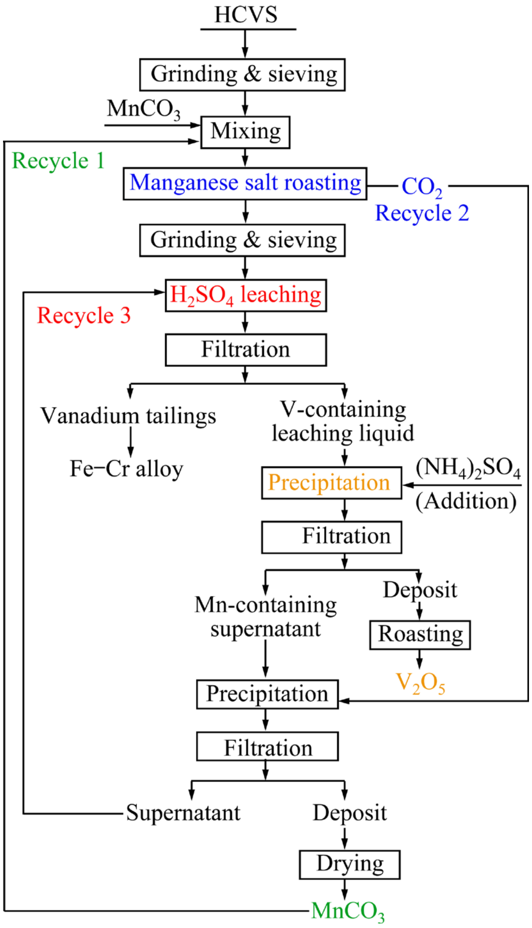

Fig. 7 Flowchart of manganese roasting−acid leaching (Adopted from WEN et al [61])

(2) The utilization rate of resources has significantly increased. The manganese element in the vanadium extraction wastewater is recovered through step-by-step precipitation, and the iron and residual vanadium in the vanadium extraction tailings are recovered in the ironmaking process of blast furnace.

(3) The cost of vanadium extraction has significantly decreased. The full recovery and recycling of additive MgO, as well as the recycling of water and ammonium salts, have reduced the consumption cost of raw materials.

However, there are still the following issues that need to be further addressed in these techniques:

(1) Removal technique is required after accumulation of impurity elements. The water resources are recycled in the vanadium extraction system, and the impurities accumulate continuously during the cycle.

(2) For the manganese roasting−acid leaching

technique, the extraction rate of vanadium is low. The laboratory implementation value is only 89%.

(3) A large amount of NaOH is added to construct the recycling path of roasting additive $MnCO_3$. Due to the presence of approximately 1 g/L NH_4^+ in the solution after vanadium precipitation, a large amount of NH_3 is generated to pollute the environment.

6 Other vanadium extraction technique

6.1 Non-salt roasting−leaching

A series of harmful gases are generated during the sodium roasting process. Based on this, many researchers proposed to use non-salt roasting−leaching technique to extract vanadium. Non-salt roasting refers to the direct use of high-temperature roasting in an oxidizing atmosphere without adding any additive to destroy the vanadium-containing phase structure, resulting in the transformation of V(III) into V(IV) or V(V) [62]. Then, vanadium is extracted by leaching in acidic/ alkaline media.

6.1.1 Non-salt roasting−sodium carbonate leaching

In order to control the generation of pollution sources from the source, LI et al [22] proposed the new technique of non-salt roasting−sodium carbonate leaching. The vanadium-rich phase is converted into $NaVO_3$ in Na_2CO_3 solution, and the vanadium extraction efficiency can reach >90%.

6.1.2 Non-salt roasting−sodium hydroxide leaching

LIU et al [63] proposed the non-salt roasting−sodium hydroxide leaching technique to extract vanadium. The main reactions ((Eqs. (22)−(25) and Eqs. (S26) and (S27) in Supporting Information) in the roasting process are as follows:

$$FeO\cdot V_2O_3+FeO+1/2O_2=Fe_2O_3\cdot V_2O_3 \quad (22)$$

$$FeO\cdot V_2O_3+1/2O_2=Fe_2O_3\cdot V_2O_4 \quad (23)$$

$$Fe_2O_3\cdot V_2O_4+1/2O_2=Fe_2O_3\cdot V_2O_5 \quad (24)$$

$$Fe_2O_3\cdot V_2O_5=Fe_2O_3+V_2O_5 \quad (25)$$

Then, the roasted sample is leached with NaOH, and the main reactions are as follows:

$$V^{5+}+8OH^-=VO_4^{3-}+4H_2O \quad (26)$$

The vanadium extraction efficiency can reach >95%, and there is no harmful gas generated during the process.

6.1.3 Non-salt roasting−ammonium bicarbonate leaching

To avoid the discharge of waste gas and wastewater from the source, LI et al [62] proposed the non-salt roasting−ammonium bicarbonate leaching technique to extract vanadium. The main reactions are as follows:

$$2Fe_2O_3+V_2O_3+8MgO+O_2=4Mg_2VO_4+2Fe_2O_3 \quad (27)$$

$$2Fe_2O_3\cdot V_2O_4+4MnO+O_2=2Mn_2V_2O_7+2Fe_2O_3 \quad (28)$$

$$4Mg_2VO_4+2V_2O_5+O_2=4Mg_2V_2O_7 \quad (29)$$

$$2Fe_2O_3\cdot V_2O_4+4MgO+O_2=2Mg_2V_2O_7+2Fe_2O_3 \quad (30)$$

Then, the roasted sample is leached in 35% NH_4HCO_3 at 50 °C for 150 min. The vanadium-rich phases are converted to water-soluble NH_4VO_3 in the leaching process, and the vanadium extraction efficiency is 85%. Then, the vanadium-containing solution is cooled and crystallized to obtain NH_4VO_3 crystals. Vanadate precipitation wastewater can be returned to the leaching process for recycling.

6.1.4 Non-salt roasting−ammonium oxalate leaching

Since ammonium oxalate is relatively stable at high temperatures and for fear of expensive and complicated ammonium control operations, LI et al [64] proposed a non-salt roasting−ammonium oxalate leaching technique. The main reactions are as follows:

$$2Fe_2O_3\cdot V_2O_4+2CaO+O_2=2CaV_2O_6+2Fe_2O_3 \quad (31)$$

$$2Fe_2O_3\cdot V_2O_4+2MnO+O_2=2MnV_2O_6+2Fe_2O_3 \quad (32)$$

$$2Fe_2O_3\cdot V_2O_4+2MgO+O_2=2MgV_2O_6+2Fe_2O_3 \quad (33)$$

Then, the roasted sample is leached in 13% $(NH_4)_2C_2O_4$ at 70 °C for 60 min. The vanadium-containing phases (CaV_2O_6, MnV_2O_6 and MgV_2O_6) are converted to NH_4VO_3 in the leaching process, and the vanadium extraction efficiency is 90%.

Compared to traditional roasting techniques, the non-salt roasting technique has significantly improved the cleanliness, as follows:

(1) The addition of additives is eliminated and the sintering of furnace materials is reduced.

(2) The roasting process is easy to control and reduces economic costs.

(3) No harmful gas is generated in the roasting process.

However, there are still a series of problems:

(1) Due to the fact that the non-salt roasting process mainly utilizes alkaline elements such as Mg and Mn inherent in vanadium slag, it is only suitable for vanadium slag with high Mg and Mn content, which restricts its industrial application.

(2) The process of vanadium extraction still

requires higher temperature and time. The vanadium extraction efficiency is low.

(3) The fluctuation of vanadium slag composition leads to unstable production.

6.2 CaO/MgO composite roasting−acid leaching

The CaO/MgO composite roasting−acid leaching technique involves roasting vanadium slag by simultaneously adding CaO and MgO [65]. Then, the roasted sample is leached with sulfuric acid, achieving the vanadium extraction. The main process is similar to that of CR−AL technique.

The presence of magnesium vanadate in roasted sample can reduce the encapsulation of calcium vanadate by the leaching reaction product (calcium sulfate), thereby improving the vanadium extraction efficiency. Theoretically speaking, the vanadium extraction efficiency of this technique should be better than that of CR−AL technique.

6.3 Ammonium sulfate roasting−sulfuric acid leaching

To extract accompanying titanium resources simultaneously in traditional roasting processes, ZHANG et al [66] proposed the ammonium sulfate roasting−sulfuric acid leaching technique to extract vanadium and titanium from vanadium slag. In order to improve the extraction efficiency of vanadium and titanium, the original vanadium slag is water-quenched to enhance its activity. The treated vanadium slag is roasted with $(NH_4)_2SO_4$. Then, the roasted sample is leached with 6 vol.% dilute sulfuric acid solution. The vanadium and titanium extraction efficiencies are 91% and 77%, respectively.

Although the ammonium sulfate roasting−sulfuric acid leaching does not require high temperatures and can simultaneously extract titanium resources from vanadium slag, in order to achieve high vanadium extraction efficiency, this technique requires activation treatment of vanadium slag. This extends the process of vanadium extraction to a certain extent.

6.4 Pre-roasting−carbothermal chlorination

DU et al [67] proposed the selective vanadium extraction technique by pre-roasting−carbothermic chlorination. After blank roasting of vanadium slag, a mixture of $VOCl_3$, $FeCl_3$, and CO_2 gas is formed through carbothermal chlorination. Pure $VOCl_3$ is collected by condensation and rectification, and then the high-purity V_2O_5 is obtained by oxidation. The main reactions are as follows:

$$\begin{aligned}&(Fe,Mn)(V,Cr,Ti)_2O_4+21/2O_2=\\&\quad 1/2Fe_2O_3+MnO+Cr_2O_3+V_2O_5+2TiO_2\end{aligned} \tag{34}$$

$$1/3V_2O_5+1/2C+Cl_2=2/3VOCl_3+1/2CO_2 \tag{35}$$

$$1/3Fe_2O_3+1/2C+Cl_2=2/3FeCl_3+1/2CO_2 \tag{36}$$

The vanadium extraction efficiency is 87.47%.

The extraction of high-purity V_2O_5 by pre-roasting−carbothermal chlorination has the following advantages:

(1) The purity of V_2O_5 products can reach up to 99.99%.

(2) The generation of highly toxic ammonia nitrogen wastewater is eliminated from the source.

(3) Chlorine gas can be recycled.

However, there are still the following issues that need to be further improved:

(1) Vanadium extraction efficiency is low. In laboratory scale, vanadium extraction efficiency is only 87%. If it is applied industrially, the vanadium extraction rate will be significantly lower than that of the existing vanadium extraction technique.

(2) The crude $VOCl_3$ obtained by fluidized chlorination is mixed with a certain amount of $FeCl_3$ gas, and 87% of V and 19% of Fe in the roasted sample enter the mixed gas. This puts forward high requirements for the control of the subsequent rectification process.

(3) The vanadium extraction tailings contain $MnCl_2$. Due to the corrosive effect of Cl element on the lining of blast furnace and converter, it is difficult to utilize the vanadium extraction tailings.

6.5 Direct oxidation of molten vanadium slag

The direct oxidation technique is to use the physical thermal effect of molten vanadium slag to directly supply oxygen to obtain high valence vanadium oxide, and add alkaline additives to generate vanadates [68]. LI et al [69] studied the sodium roasting of molten vanadium slag, and the vanadium extraction efficiency could reach more than 90%. SONG et al [9] studied the calcification roasting of molten vanadium slag, and found that the vanadium extraction efficiency could reach 90%.

Direct oxidation of molten vanadium slag for vanadium extraction utilizes the physical heat of molten vanadium slag, eliminating the traditional roasting step and saving energy consumption. According to calculations, every 1000 kg of vanadium slag can save 1.85×10^6 kJ of energy [70]. However, the principle of roasting−leaching is similar to that of traditional roasting−leaching, so the problems of environment and resource utilization of traditional roasting−leaching still exist in the direct oxidation of molten vanadium slag.

6.6 Direct leaching technique

With the rapid development and continuous improvement of hydrometallurgical technique, many researchers begin to study the low-temperature hydrometallurgical technique to extract vanadium to reduce a series of environmental hazards caused by the use of high-temperature oxidation roasting process and the high energy consumption.

6.6.1 Pressure acid leaching

In the direct acid leaching process, the solid product produced after a certain time of the leaching reaction wraps around the unreacted nucleus, thus reducing the reaction rate. Therefore, in order to create favorable kinetic conditions for vanadium extraction, ZHANG et al [71] proposed the pressure acid leaching technique for vanadium extraction and found that the vanadium extraction efficiency can reach 97.69%.

6.6.2 Electrooxidation acid leaching

During the electrooxidation acid leaching process, the addition of electrodes in the leaching container can achieve directional migration of metal charged ions under the action of an electric field, accelerating the diffusion and dissolution of metal ions from the silicate and spinel phases. LIU et al [72] proposed the electrooxidation acid leaching technique of vanadium slag. The reactions that occur during the leaching process are shown in Eqs. (S28)−(S37) in Supporting Information. With leaching time of 4 h, H_2SO_4 concentration of 40 wt.%, L/S ratio of 4:1 (mL/g), electrode spacing of 20 mm, working potential of 2.8−3.0 V, and anode current of 0.4 A at 75 °C, the vanadium extraction efficiency of 75.64% was obtained.

6.7 Bioleaching

Bioleaching technique, as a new metallurgical technique, has attracted more and more attention of researchers [73−77]. The technique is initially applied to the leaching of copper ore [78,79]. Inspired by this, MIRAZIMI et al [80] began to focus on using bioleaching technique to extract vanadium. Vanadium slag is roasted with Na_2CO_3, promoting the transformation of vanadium-containing phase into more soluble phases. Then, the roasted sample is leached in fungi and bacteria. The results show that bacteria are beneficial for vanadium extraction, and the vanadium extraction efficiency is above 80%, while the vanadium extraction efficiency is about 70% after 20 d in fungal systems.

Although the bioleaching is a relatively green and clean vanadium extraction technique, the bioleaching process must create suitable temperature, pH and other conditions for the growth of microorganisms. In addition, microorganisms not only react slowly but also take a long time, making the bioleaching technique difficult to apply on a large scale.

7 Conclusions

So far, the SR−WL is the most commonly applied technique for vanadium extraction in industry. The CR−AL technique and the sub-molten salt technique are cleaner vanadium extraction techniques, both of which are initially applied in industry. Although the cleanliness level of these vanadium extraction techniques has been successively improved, the problems of high energy consumption, long process, low recovery rate, low selectivity, and large production of wastewater still exist. The magnesiation roasting−acid leaching technique realizes the cycling of roasting additive, water, ammonium sulfate, and ammonia gas, which achieves the near-zero discharge and is thus more in line with the development direction of greenization, but has not realized industrial application yet. With the increasing global concern on resource and environment, green vanadium extraction from vanadium slag is definitely the development trend. In order to promote the greenization level of vanadium extraction, future studies could focus on the following aspects:

(1) Comprehensive resource utilization of vanadium slag, focusing on the extraction of not only vanadium but also other valuable resources (Fe, Mn, Ti, Cr, etc);

(2) Microscopic conversion and migration mechanisms of valuable components during

vanadium extraction, not remaining at the macro level;

(3) Completing the thermodynamic database of vanadium slag system, including the Gibbs free energy, solubility, phase-transition temperature, activity, etc of relevant components;

(4) Roasting kinetics of vanadium slag, which can guide the amplification and optimization of industrial product line of newly developed green vanadium extraction technique.

CRediT authorship contribution statement

Jie CHENG: Writing − Original draft; **Hong-yi LI:** Conceptualization, Writing − Review & editing, Funding acquisition; **Dai-bo GAO:** Data curation; **Xin-mian CHEN:** Visualization; **Dong HAI:** Data curation; **Jiang DIAO:** Supervision; **Bing XIE:** Project administration; **Fu-sheng PAN:** Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supporting Information

Supporting Information in this paper can be found at: http://tnmsc.csu.edu.cn/download/20-p1306-2023-0961-Supporting_Information.pdf.

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中国钒渣提钒的绿色化之旅

成洁[1]，李鸿义[1,2]，高代波[1]，陈新勉[1]，海栋[1]，刁江[1,2]，谢兵[1]，潘复生[1,2]

1. 重庆大学 材料科学与工程学院，重庆 400044；
2. 重庆大学 国家镁合金材料工程技术研究中心，重庆 400044

摘　要：中国是世界上最大的钒制品产销国，主要的提钒原料是冶炼钒钛磁铁矿所得到的钒渣。在过去的 30 年里，我国的钒渣提钒技术逐步向绿色化发展。该综述系统总结了这些发展，并将其划分为 3 个发展阶段。早期阶段着重于高效提钒，如钠化焙烧−水浸技术。进阶阶段为清洁提钒，包括钙化焙烧−酸浸技术和亚熔盐技术。高级阶段是绿色提钒，如镁化焙烧−酸浸技术。按照不同发展阶段，从多角度详细介绍了已工业化应用和文献报道的各种钒提取技术的机理及优缺点。最后，指出钒提取技术的未来发展方向，旨在为全球绿色提钒技术的发展提供借鉴。

关键词：钒渣；钒；绿色提取；焙烧；浸出

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