

# A review on the extraction of vanadium pentoxide from primary, secondary, and co-product sources

Amirreza Nasimifar<sup>a</sup>, Javad Vazifeh Mehrabani<sup>a,\*</sup>

<sup>a</sup> Department of Mineral Processing, Faculty of Mining Engineering, Sahand University of Technology, Sahand New Town, Tabriz, Iran.

## Article History:

Received: 13 February 2021.

Revised: 31 March 2022.

Accepted: 27 May 2022.

## ABSTRACT

Vanadium is a strategic metal and its compounds are widely used in industry. Vanadium pentoxide ( $V_2O_5$ ) is one of the important compounds of vanadium, which is mainly extracted from titanomagnetite, phosphate rocks, uranium-vanadium deposits, oil residues, and spent catalysts. The main steps of vanadium extraction from its sources include salt roasting, leaching, purification, and precipitation of vanadium compounds. In the hydrometallurgical method, first, the vanadium is converted to a water-soluble salt by roasting, and then the hot water is used to leach out the salt-roasted product and the leach liquor is purified by chemical precipitation, solvent extraction, or ion exchange processes to remove impurities. Then, a red cake precipitates from an aqueous solution by adjusting the conditions. To provide high pure vanadium pentoxide, it is necessary to treat the filtered red cake in an ammonia solution. So, ammonium metavanadate (AMV) is precipitated, calcined, and flaked to vanadium pentoxide. In the pyrometallurgical method, vanadium-containing concentrate is smelted, and by forming titanium-containing slag and molten pig iron, oxygen is blown into pig iron in a converter or shaking ladles, and vanadium is oxidized to produce vanadium-rich slag. In the next step, the slag is roasted and treated by the hydrometallurgical process. In this paper, the industrial processes and novel developed methods are reviewed for the extraction of vanadium pentoxide.

**Keywords:** Vanadium pentoxide, Extraction, Roasting, Leaching, Process.

## 1. Introduction

### 1.1. Vanadium and its applications

Vanadium is a gray metallic element with atomic number 23 in the periodic table [1]. This element was first discovered in 1801 by Manuel del Rio. Then, Sefstrom rediscovered vanadium in 1830 and isolated it from the Swedish iron mine, Taberg [1]. Vanadium is the 22nd most abundant element with an average concentration of 159 g/ton and is widely distributed in the earth's crust [2,3] with V(III) replacing some minerals [4].

The main vanadium products include ferrovanadium, vanadium pentoxide, vanadium trioxide, vanadium nitride, and pure metal [5]. Table 1 introduces the main properties of the most common vanadium oxides and vanadates [6]. Vanadium pentoxide powder and flake ( $V_2O_5$ ) is the most common form of vanadium oxide. In addition, the vanadates such as ammonium metavanadate (AMV), sodium metavanadate, and sodium orthovanadate are other common forms of vanadium [3]. For the first time, vanadium has been used as an alloying element in the iron and steel industry, which consumes 85% of the world's vanadium production [2]. Figure 1 shows the distribution of vanadium to its final applications [2]. Adding small amounts of vanadium, significantly increase the tensile strength and toughness of nickel/vanadium, chromium/vanadium, and iron/vanadium (ferrovanadium) alloys [2]. Titanium alloying with vanadium improves the properties of titanium [7], which is used in combination with aluminum and vanadium in missiles, nuclear reactor components, and jet engines [2]. About 10% of vanadium consumption is related to the manufacture of aircraft alloys [7], and there is no alternative to vanadium in the manufacture of these alloys in the aerospace industry [2]. In addition, vanadium pentoxide is used as a catalyst for the conversion of sulfur dioxide to trioxide in the

production of sulfuric acid, and as a chemical in the preparation of polyester and fiberglass resins [2]. In medical studies, vanadium compounds have been proposed for the treatment of diabetes, cancer, and other diseases [8], and these diverse chemical applications consume 5% of vanadium [2]. The latest developments in the use of vanadium are the storage of energy in newly developed batteries (vanadium redox battery (VRB)) [2,4], the production of glasses, the filtering of windows against UV rays, and the production of vitamin A tablets [9].

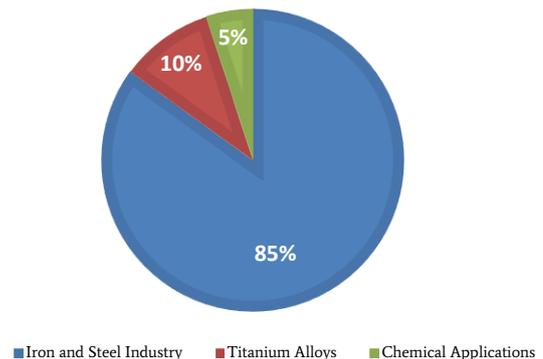


Figure 1. Distribution of vanadium usage [2].

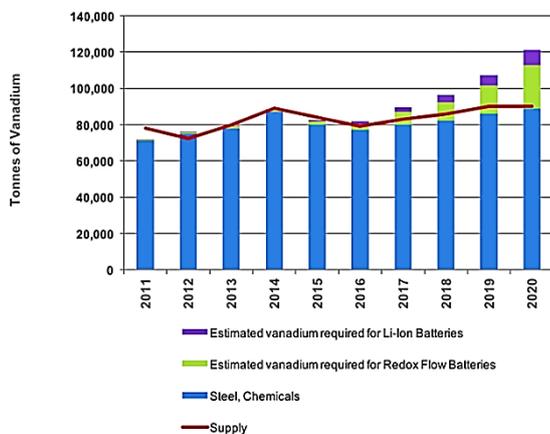
\* Corresponding author. Tel/Fax: +98 4133459306, E-mail address: mehrabani@sut.ac.ir (J. Vazifeh Mehrabani).

**Table 1.** Physical and chemical properties of most common vanadium oxides and vanadates [6].

Compound	Molecular formula	Color	Melting point	Solubility
Vanadium pentoxide	V <sub>2</sub> O <sub>5</sub>	Orange-yellow	650-690	Water: slightly Acid: soluble Alkali: Soluble
Vanadium trioxide	V <sub>2</sub> O <sub>3</sub>	Dark	1970-2070	Water: none Acid: HF and HNO <sub>3</sub> Alkali: none
Vanadium tetraoxide	VO <sub>2</sub>	Blue	1545-1967	Water: none Acid: soluble Alkali: Soluble
Vanadium dioxide	VO	Light gray	1790	Water: none Acid: soluble Alkali: none
Sodium metavanadate	NaVO <sub>3</sub>	Colorless	630	Soluble in water
Ammonium metavanadate	NH <sub>4</sub> VO <sub>3</sub>	Canary yellow	Decomposition at 200	Soluble lightly in water
Sodium pyrovanadate	Na <sub>4</sub> V <sub>2</sub> O <sub>7</sub>	Colorless	632-654	Soluble in water
Sodium vanadate	Na <sub>3</sub> VO <sub>4</sub>	Colorless	850-856	Soluble in water
Potassium metavanadate	KVO <sub>3</sub>	Colorless	-	Soluble in hot water
Calcium metavanadate	CaV <sub>2</sub> O <sub>6</sub>	-	778	-

## 1.2. Global supply and demand of vanadium

Vanadium consumption is heavily dependent on the iron and steel industries [5]. Figure 2 shows the growth of vanadium demand from 2011 to 2020 [10]. In addition, strict regulations for the use of high-strength steel increased the demand for vanadium, which is expected to increase significantly in the coming years for the development of high-performance VRB and lithium batteries [4].

**Figure 2.** The growth of vanadium demand [10]

In 2020, global vanadium production was 100,012 metric tons of vanadium (MTV) which 94,800 MTV of vanadium was consumed in steel (Table 2) [11]. China consumed 61,050 MTV in 2020, an increase of 14% as compared to 2019 [11].

Global reserves of vanadium are about 38 million tons of metal. At present, China, Russia, and South Africa are the world's leading producers of vanadium [12], with 60%, 17%, and 7% of global vanadium supply in 2020, respectively (Figure 3) [13].

40% of vanadium produced in China is recovered through vanadium slag, which is a co-product of titanomagnetite and iron ores [13,14]. Vanadium pentoxide and ferrovandium are the most common trade products [13]. Significant amounts of ferrovandium are also produced from petrochemical wastes and spent catalysts in Japan, the United States, and the European Union, which import large quantities of vanadium-containing slag from China and Russia [5]. However, the

cost of producing vanadium from secondary sources is higher than from primary sources and slags [13].

## 1.3. Vanadium sources

The global reserves for vanadium production are included in primary, secondary, and co-product sources [13]. Table 3 indicates the vanadium general resources. Also, Figure 4 shows global vanadium production by source in 2020. It illustrates that about 18%, 10% and 72% of vanadium have been produced from primary, secondary, and co-product sources respectively.

### 1.3.1. Primary sources of vanadium

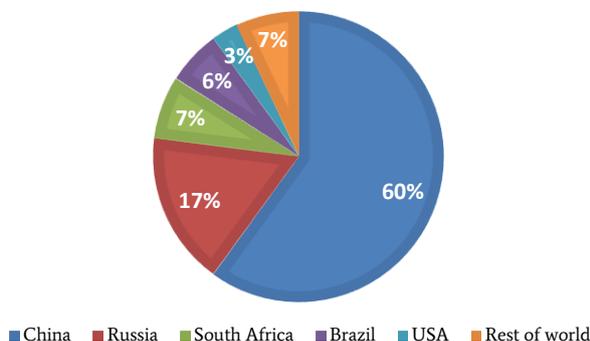
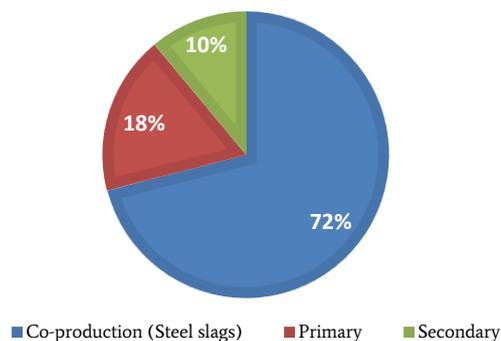
The primary source is considered to be ore or concentrate, which is used directly to produce vanadium or its compounds. In nature, vanadium is found in more than 65 different minerals such as patronite, vanadinite, carnotite, and roscoelite [1]. The principal vanadium minerals are listed in Table 4 [7,21].

In the early 1900s, vanadium was mined only from the patronite mines of Peru. Then, roscoelite deposits and uranium-vanadium-bearing sedimentary sources were explored [7]. From the mid-1950s, vanadium production from titanomagnetite resources increased sharply [7]. Nowadays, generally, vanadium-bearing titanomagnetite with above 1 wt.% V<sub>2</sub>O<sub>5</sub> are common primary sources for vanadium extraction [7,15]. Studies have shown that vanadium is primarily present in the V(III) form in volcanic rocks. Since the ionic radius of V(III), Mn(III), Fe(III) and Ti(III) are similar, they can form polymetallic ore [22]. X-ray absorption near-edge spectroscopy (XANES) has shown that vanadium is mainly present in the V(III) form in titanomagnetite deposits [4]. Titanomagnetite ore which contains vanadium, titanium, and iron [23], was discovered first in Russia, China, and South Africa. Vanadium is often associated with iron oxides in the form of coulsonite (FeV<sub>2</sub>O<sub>4</sub>) [23]. Therefore, iron and titanium deposits can be the main sources of vanadium [4,24].

In China, another important primary source of vanadium is stone coal (also called black shale [14] and sometimes carbonaceous shale [25]), which accounts for 87% of China's domestic vanadium reserves [12,14]. The grade of vanadium in stone coal is generally in the range of 0.13 to 1.2 % [15]. In stone coal, V(III) is usually predominant [12]. Except in China, other countries have very little interest in the study of vanadium extraction from stone coal due to limited resources [12].

**Table 2.** Vanadium market in 2019 and 2020 [11].

Year	China				World			
	Vanadium consumption (MTV)		Vanadium production (MTV)		Vanadium consumption (MTV)		Vanadium production (MTV)	
	2019	2020	2019	2020	2019	2020	2019	2020
Total	53,499	61,050	63,938	59,284	102,008	101,800	102,365	100,012
Steel	50,200	58,000			93,100	94,800		
Titanium alloys	965	750			3,883	1,950		
Chemicals	1,240	1,100			3,640	3,350		
Energy storage	1,094	1,200			1,385	1,700		

**Figure 3.** Global vanadium production by country in 2020 [13].**Figure 4.** Global vanadium production by source in 2020 [13].**Table 3.** General resources of vanadium production

Resources type	Resources Name	V <sub>2</sub> O <sub>5</sub> Content (%)
Primary	Natural ore	1.2-81 [7]
	Vanadium-bearing titanomagnetite	0.39-3.21 [15]
	Stone coal	0.13-1.2 [15]
Secondary	Ferrophosphorus	3-11% [16]
	Fly ash	2.5-40% [17]
	Vanadium-bearing uranium ore	0.25-2% [18]
	Spent catalysts	0.5-30% [18,19]
	Bayer red mud	0.18-0.7% [20]
Co-product	Vanadium slag	6-24% [5]

**Table 4.** Vanadium minerals [7,21]

Mineral name	Chemical formula
Rescoelite	KV <sub>2</sub> (OH) <sub>2</sub> AlSi <sub>3</sub> O <sub>10</sub>
Carnotite	K <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> V <sub>2</sub> O <sub>8</sub> ].3H <sub>2</sub> O
Mottramite	Pb(Cu, Zn)[(OH)(VO <sub>4</sub> )]
Vanadinite	Pb <sub>2</sub> [(Cl)(VO <sub>4</sub> ) <sub>3</sub> ]
Descloizite	Pb(Zn, Cu)[(OH)(VO <sub>4</sub> )]
Tyuyamite	Ca[(UO <sub>2</sub> ) <sub>2</sub> (V <sub>2</sub> O <sub>8</sub> )].5 - 8H <sub>2</sub> O
Patronite	VS <sub>4</sub> or V <sub>2</sub> O <sub>5</sub>

### 1.3.2. Secondary and Co-product sources of vanadium

A secondary source is a by-product of another process that contains a significant amount of vanadium. Due to the lack of natural ores of vanadium such as vanadinite and carnotite, vanadium is mainly supplied as a by-product from other sources [23].

Vanadium, like titanium, can be recovered from co-product slag, derived from iron processing for steel production during the smelting of titanomagnetite ores [4]. A vanadium slag contains approximately 14% vanadium [7]. About 88% of worldwide vanadium is mined from titanomagnetite often vanadium slag fed to the vanadium processing

plants [26]. For economic extraction of vanadium, it is necessary the vanadium in the ore to be enriched into the slag by smelting processes, when the V<sub>2</sub>O<sub>5</sub> grade is lower than 1 wt.% [15]. Vanadium is present in the form of stable spinel involved with the olivine phase, or iron silicates in the slag, which cannot be used directly to extract vanadium [16].

Many vanadium-containing uranium deposits are in the form of uranyl-vanadate minerals such as carnotite, from which vanadium is extracted as a by-product of uranium mining [4]. Another significant secondary source of vanadium is ferrophosphorus [4]. Some phosphate rocks, which contain small amounts of vanadium, are concentrated in the ferrophosphorus by-product during the smelting process in the production of phosphorus and phosphate fertilizer, and their grade can be about 3 to 11% [27].

Crude oil contains valuable metals such as vanadium. The concentration of vanadium in crude oil varies from 10 ppm to 1400 ppm [7], and its amount in Iran is lower than in other places of the world. The physical, chemical, and biological methods are used to separate metals from crude oil, but they are expensive and pollute the environment [28-30]. The most important physical processes for removing metals from crude oil are distillation, membrane methods, and solvent extraction [31]. Also, most chemical methods for removing metals such as vanadium from crude oil are included in acid or base treatment, selective oxidation, and catalytic methods (removal of metals through the substrate of adsorbent catalysts) [31]. Biological methods (using enzymes and microorganisms to remove vanadium compounds such as Bacillus Megaterium, Catharanthus Roseuse, and Pseudomonas Azelacia) have been considered in recent years and related studies are ongoing [31]. However, burning some crude oils, such as Venezuelan oil in power plants, produces ashes with high levels of vanadium and other precious metals [17]. Studies on the chemical composition of various ashes have shown that they contain 2.5 to 40% vanadium pentoxide [17]. The extraction of vanadium from fly ash has attracted attention since the 1960s [32]. The ashes from oil burning are important secondary sources of vanadium after concentrations of the vanadium ores and slags [17].

Other secondary sources of vanadium are residue from the bauxite concentration process and spent catalysts in the petrochemical industries [7]. Red mud is a solid residue from bauxite ore in alumina

production, usually containing vanadium, titanium, and other precious metals, which contain 0.1 to 0.4 wt.% of vanadium [20]. In addition, some bauxite deposits contain large amounts of vanadium, but vanadium production is more expensive than slag [13]. The carbon adsorption and desorption process include solubilization of vanadium, adsorption on activated charcoal, desorption, and precipitation of vanadium pentoxide, has been used mainly on a laboratory scale for extracting vanadium from red mud, and it is not clear that this process can be used in industrial and economic scale [33-35].

Spent catalysts have good potential for extracting valuable elements (Ni, V, Mo, Co, etc.) due to the depletion of primary resources mines, increasing vanadium demand by the industry, and landfilling environmental problems as hazardous wastes [19, 36, 37]. The hydrometallurgical (acid or alkali leaching and solvent extraction processes) in the combination of roasting and bio-hydrometallurgical (bacterial leaching based on the ability of microorganisms, bacteria, or fungi as leaching reagents) methods have been reported for the extraction of vanadium from the spent catalysts at room temperature and atmospheric pressure [38-42]. However, further studies are needed to develop a process that considers low waste generation, safe waste disposal, low costs, and other economic, and environmental benefits [19, 42].

In Iran, most attention is focused on steelmaking slags and secondary sources. Studies have been performed on its recovery from the converter slag in steelmaking and from heavy fuels [43], which can be referred to as the extraction of vanadium from converter slag [44, 45], the purification of the leached vanadium solution from the converter slag [46] and extraction of vanadium from the boiler fuel ash [47,48]. Also, the amount of vanadium pentoxide has been reported as about 1.9% wt.% in converter slag in Mobarake steel company [49]. Other important sources of vanadium in Iran are Kahnooj titanomagnetite concentrate with a grade of 1.7% [50] and Iranian iron ore in Choghart, Seh Chahun, and Chahgaz [43]. The amount of vanadium pentoxide in Choghart iron ore has been reported in the range of 0.3 to 0.5% [51]. Saghand ore in Yazd also contains vanadium compounds; the amount of vanadium pentoxide has been reported in the range of 0.3 to 0.4 wt.% [52].

In the present paper, the commonly used processes in industry and novel environmentally friendly methods are investigated for the extraction of vanadium pentoxide.

## 2. Industrial vanadium pentoxide production processes

The processing of vanadium greatly depends on the nature of the feed, but all processes have a few common features [4], which include the steps of physical beneficiation, salt roasting, leaching, solution purification, and precipitation [4, 5, 18]. Figure 5 shows the general flowsheet of vanadium extraction [18].

### 2.1. Physical beneficiation

In the mineral processing industry, it is common to prepare a concentrate before hydrometallurgical and pyrometallurgical operations to increase the grade of the valuable material, and significantly remove the gangue material. Therefore, the production of concentrate from the primary sources before hydrometallurgical and pyrometallurgical operations will be useful. Generally, the use of physical beneficiation for all vanadium sources will not be successful due to the complexity of the source structure and the low specific gravity of the vanadium compounds [18]. However, the mineralogical and textural characteristics will determine the amenability of resources to beneficiation [53]. Among vanadium sources, concentrate is mainly produced from the titanomagnetite ores. However, the concentrate is prepared when vanadium-bearing magnetite is separated from ilmenite [5,54].

Titanomagnetite ore is a common and valuable polymetallic mineral that mainly contains iron, titanium, and vanadium [55]. The major structure of vanadium-bearing titanomagnetite includes ilmenite ( $\text{FeTiO}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) [53, 55]. Titanomagnetite ore is mainly used to produce iron, and titanium concentrates [55]. During the

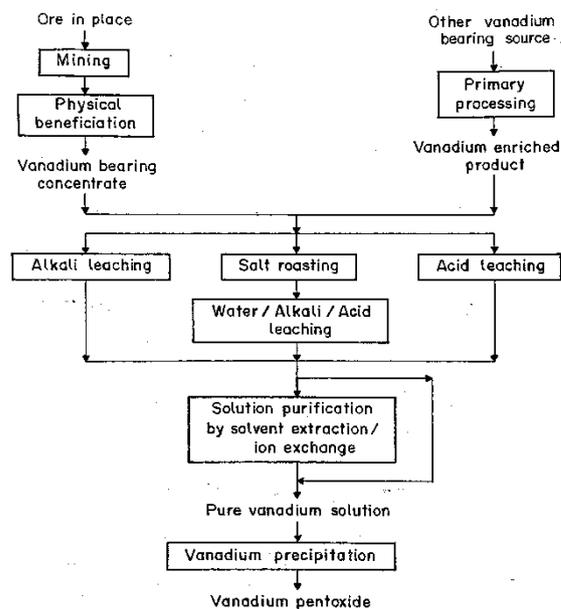


Figure 5. General flowsheet of vanadium extraction from the vanadium sources [18].

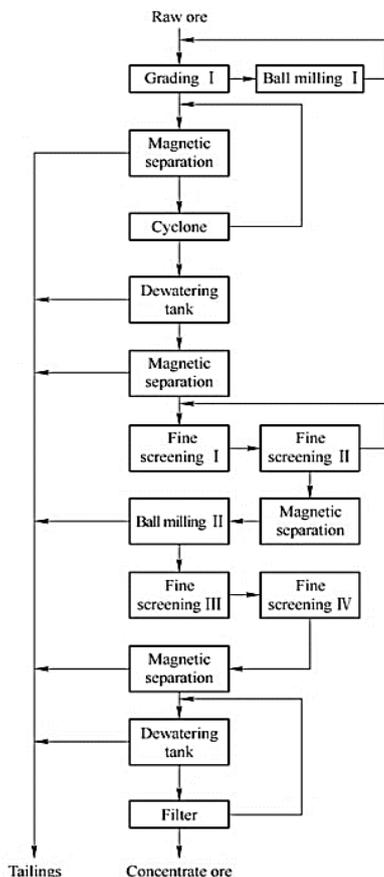
formation of titanomagnetite, magnetite precipitated along with ilmenite, where the associated vanadium is isomorphous with iron minerals. Thus, most of the vanadium enters the iron concentrate during ore concentration processes [55]. Generally, the dressing of the titanomagnetite ores is included primary and secondary crushing, grinding, and magnetic separation stages [53]. In typical beneficiation methods, first, the extracted ore from the mine is crushed and milled by major equipment such as jaw crushers, hammer crushers, and ball mills. In the next step, vanadium-bearing iron concentrate is obtained through magnetic separators [55].

Depending on the particle size of the ore, magnetic separation is associated with either continuous or batch grinding. One or two stages of continuous grinding and magnetic separation can be used for coarse ores with high iron content (only one stage of grinding is performed for the ore with particle sizes larger than 0.2-0.3 mm). However, batch grinding is suitable for ores with fine particle size and low iron content [55]. In addition, the screening and grading (such as vibrating screens, hydro cyclones, and spiral classifiers) steps improve the grade of iron concentrate. Figure 6 is shown a typical flowsheet for the batch grinding, magnetic separation, and fine screening process [55].

In addition, physical beneficiation such as gravity separation is tested in the treatment of the low-grade vanadium-bearing stone coal ores. In these ores, Vanadium mainly exists in mica, and theoretically, can be concentrated [56]. In gravity separation, the ore is first crushed and milled to 75 microns (<200 mesh). After gravity separation and classifier overflow, the vanadium concentrate is collected with a particle size of less than 0.03 mm. In this process, the recovery of vanadium is 50% [56]. To increase the recovery of vanadium, the gravity separation process is combined with the flotation process, in which sodium hexametaphosphate, lauryl sodium sulfate, and pine camphor oil were used as the flotation adjustment, collecting, and frothing reagents, respectively [56]. All of the aforementioned processes are not applied on an industrial scale due to poor recovery of the vanadium, which is associated with low vanadium content and complex stone coal characters [56].

### 2.2. Salt roasting

The principle of vanadium recovery is the oxidation of water or acid-insoluble V(III) to acid-soluble V(IV) or water-soluble V(V) compounds. In other words, V(III) in vanadium spinel ( $\text{FeV}_2\text{O}_4$ ) reacts with oxygen and is oxidized to V(V) by reactions (1)-(4) as the



**Figure 6.** Typical separation processes include batch grinding, magnetic separation, and fine screening [55].

temperature arose. Then, V(V) and roasting additive formed soluble sodium metavanadate ( $\text{NaVO}_3$ ) [4] based on reactions (5)-(9) [4,55].

Therefore, the roasting process is used to enhance vanadium recovery [26]. The first roasting technology is roasting with sodium salts such as sodium chloride, sodium sulfate, and sodium carbonate as roasting additives [17]. During the roasting, one of the salts or a mixture of them can be used [4,18].



The efficiency of vanadium extraction using sodium sulfate is much higher than sodium chloride, and sodium carbonate [57]. However, it requires high temperatures [2, 57]. The use of sodium carbonate is common in the industry due to its low price [12], prevention of toxic and corrosive gases [4, 26, 57], selective roasting, and relatively low roasting temperature [23]. Sodium carbonate roasting at 800°C and following water leaching for 120 minutes, about 87.9% of vanadium could be leached out from a high-chromium vanadium slag [26]. It should be noted that sodium carbonate may affect the recovery of vanadium by forming compounds of silica, aluminum, and other elements [50]. Chemical reactions of sodium salt additives are present in Table 5 [5, 57]. In recent years, roasting with sodium hydroxide salt has been proposed, which has advantages over carbonate roasting [16,58-65]. In addition to sodium salts, Lee et al. have investigated slag roasting with potassium salts under certain conditions the roasting efficiency of vanadium increased significantly according to the reaction (9) [63]. Recently, roasting with manganese and magnesium salts is proposed to extract vanadium from the vanadium slag with the aim of cleaner production [16,64].

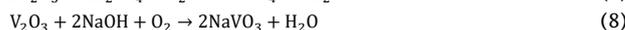
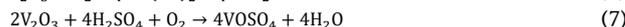
### 2.3. Leaching

Roasted material is leached out by water, acid, or alkaline reagent to dissolve vanadium [5]. The dissolving reagents can be sulfuric acid ( $\text{H}_2\text{SO}_4$ ), water, or an alkali such as sodium carbonate. Water can selectively leach out and separated water-soluble sodium vanadate from water-insoluble compounds such as calcium, magnesium, and iron vanadates by reaction (10) [5]. Also, about 65-85% of vanadium is recovered in solution by water leaching [18]. However, impurities such as silicon, titanium, chromium, and aluminum can react with sodium carbonate and form water-soluble compounds that decrease vanadium recovery [4].



The acid leaching can dissolve the complex vanadium compounds which are formed during the roasting process and increase the leaching efficiency (10-15% more vanadium recovery over the water leaching from the roasted uranium-vanadium ore) [18], but other elements such as iron, aluminum, and magnesium can be dissolved in an acidic solution with vanadium, and the leach liquor contains a large number of impurities and makes vanadium separation difficult. Alkali reagent has been suggested for selective leaching of vanadium over acid leaching [18,65]. However, the extraction efficiency of alkali leaching is lower than acid leaching [65]. Table 6 presents a comparison of the different reagents and reactions (1)-(5) for vanadium leaching.

There are methods for direct leaching of vanadium ores through reactions (6)-(8) [4, 15, 66], but they are rarely used due to environmental problems, the production of large amounts of waste [5], strong corrosion (the challenge in selecting equipment and maintenance), and the need to apply intensified conditions [4, 15].



### 2.4. Leach liquor purification

During the leaching process, impurities such as silica, aluminum, and iron can be dissolved with vanadium, which must be removed before vanadium is recovered [4]. Sometimes, selective separation of valuable elements from the solution is necessary for this purpose [19]. Three methods of purification are chemical precipitation, solvent extraction, and ion exchange. When the leach liquor impurities are high and vanadium concentration is low, solvent extraction and ion exchange method are used to treat [4,9, 26]. Different studies have focused on vanadium recovery using solvent extraction with different organic extractants [67-70]. Ion exchange resins are usually used to separate vanadium from neutral and alkaline solutions [20]. However, there have been reports of vanadium recovery in acidic media [71, 72]. In addition, the use of the chemical precipitation method and resins are not desirable to separate vanadium and iron from acidic solutions [73]. In previous studies, the 2-Ethylhexyl phosphoric acid mono 2-Ethylhexyl ester (P507) or also known as EHEHPA, the Di-(2-Ethylhexyl) phosphoric acid (P204) or also known as DEHPA, the Secondary carbon primary amine (N1923), and the Bis(2,4,4-Trimethylpentyl) phosphoric acid (Cyanex 272) are used for vanadium extraction from acidic leach liquors and the Weakly basic anionic resin (D314), Strongly basic anionic (D296), Chelating (DDAS, CW-2, CUW), and Strongly acidic cationic (SK1B) resins are used for vanadium extraction from the complex vanadium solutions [68,74-80]. The extraction method is widely used in the vanadium industry [20]. The advantages of the solvent extraction method include the high rate of extraction, high selectivity, large operating capacity, high-quality product, lower cost, and continuous operation [24,73]. But the advantages of this method are environmental problems (flammable and toxic organic solvents), time-consuming (Complex operational regenerations and procedures), and chemical decay of extractants in contact with V(V) [80].

In addition, studies have shown when the concentration of Fe(III) in the leach liquor is low and V(IV) is predominant in the solution due to weak extraction of V(V) and poor selectivity for V(IV) vs Fe(III), solvent

**Table 5.** Chemical reactions of salt roasting [5,57,63].

roasting additive	Chemical reactions	temperature
Sodium chloride (NaCl) with vapor	$2\text{NaCl} + \text{H}_2\text{O} + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + 2\text{HCl} \uparrow$ (5)	800-900 °C
Sodium chloride (NaCl) without vapor	$2\text{NaCl} + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{Cl}_2 \uparrow$ (6)	800-900 °C
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ )	$\text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{CO}_2 \uparrow$ (7)	900-1200 °C
Sodium sulfate ( $\text{Na}_2\text{SO}_4$ )	$\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 \rightarrow 2\text{NaVO}_3 + \text{SO}_3 \uparrow$ (8)	1200-1230 °C
Potassium sulfate ( $\text{K}_2\text{SO}_4$ )	$\text{k}_2\text{SO}_4 + \text{V}_2\text{O}_5 \rightarrow 2\text{kVO}_3 + \text{SO}_3 \uparrow$ (9)	900 °C

**Table 6.** General comparison of vanadium leaching by different reagents.

Leaching reagents	Description	Reference
<b>Water</b>	-The most selective, mature, economical, and industrial method, pH=7-8. -Main impurities in the solution: Fe, Cr, Mn, Si, P -Sodium vanadate can be leached out.	[15, 18]
<b>Alkali</b>	-Sodium carbonate, sodium bicarbonate, or sodium hydroxide are used as leaching Reagents. -Widely used in the treatment of high lime uranium-vanadium ores, boiler ash, fly ash and spent catalyst. -Non-effective but selective -Direct alkali leaching is used in the treatment of secondary sources such as fly ash. -Main impurities in the solution (using sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) reagents): Mg, Si, etc. -Main impurities in the solution (using sodium hydroxide (NaOH) reagent): Cr, Si, etc. -Almost all vanadates formed in the roasting process such as sodium vanadate can be leached out by a strong alkali reagent (NaOH). * $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 + 4\text{NaOH} \rightarrow 2\text{Na}_3\text{VO}_4 + 2\text{H}_2\text{O}$ (11) -Calcium vanadate, magnesium vanadate, and manganese vanadate can be leached out by weakly alkali reagents ( $\text{Na}_2\text{CO}_3$ , $(\text{NH}_4)_2\text{CO}_3$ and, etc.) by below reactions: * $\text{Ca}_3\text{V}_2\text{O}_8 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 2\text{Na}_3\text{VO}_4$ (Calcium vanadate) (12)	[14, 15, 18, 26]
<b>Acid</b>	-Producing a large number of impurities in the leaching solution. Main impurities in the solution (using a sulfuric acid reagent): Fe, Mn, Si, Ca, P, etc - $\text{H}_2\text{SO}_4$ acid is widely used. -Non-selective but effective -Direct acid leaching is used in the treatment of uranium-vanadium ores and fly ash. -Widely used in the treatment of uranium-vanadium ores, boiler ash, fly ash, and phosphate rock. -Almost all vanadates formed in the roasting process can be leached out by strong acids ( $\text{H}_2\text{SO}_4$ and, etc.) by the below reactions: * $\text{NaVO}_3 + \text{H}^+ \rightarrow \text{VO}_2^+ + \text{Na}^+ + \text{H}_2\text{O}$ (Sodium vanadate) (13) * $\text{Mg}_2\text{V}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 \rightarrow (\text{VO}_2)_2\text{SO}_4 + 2\text{MgSO}_4 + 3\text{H}_2\text{O}$ (Magnesium vanadate) (14) * $\text{Ca}_3\text{V}_2\text{O}_8 + 4\text{H}_2\text{SO}_4 \rightarrow (\text{VO}_2)_2\text{SO}_4 + 3\text{CaSO}_4 + 4\text{H}_2\text{O}$ (Calcium vanadate) (15)	[15, 16, 18, 26]

extraction is the best method for purification of the solution (Especially with a higher acidity) by organophosphorus extractants such as P204, P507, and Cyanex 272 [20, 80]. Therefore, V(V) in leach liquor should be reduced to V(IV) and V(V) before solvent extraction and precipitation of vanadium pentoxide which causes the complex and costly purification process [80]. However, amine extractants such as Aliquat 336 can be separated V(V) from the solution over a wide pH range (1.5-12). The organophosphorus and amine extractants are stripped by pure acid and alkaline solutions respectively [18,80].

Solvent extraction and ion exchange methods are mainly used for the purification of stone coal and spent catalyst leach liquors [15,80]. In comparison with solvent extractions, the ion exchange method is used in small-scale applications and it has good vanadium separation efficiency but its disadvantages are long exchange cycles and lack of a convenient exchange system for industrial production [80].

Chemical precipitation is a common and industrial method for removing relatively simple impurities (Especially containing low iron and aluminum content) from the alkaline leach liquor of titanomagnetite concentrate or slags obtained by the sodium roasting-water leaching process. The metal cations in the leach liquor are mainly  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  which can be hydrolyzed and separated by adjusting the pH value to 6.5-7.5, 7.8, and 8.8 respectively. Also, the anions such as  $\text{CrO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  are separated by adding the precipitation additive ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) as  $\text{MgCrO}_4$ ,  $\text{MgSiO}_3$ , and  $\text{Ca}_3(\text{PO}_4)_2$  at 90 °C. Easy operation, low cost, and high capacity are the advantages of the chemical precipitation process over solvent extraction and ion exchange methods. but the vanadium concentration must be high in leach liquor [80]. In addition, chemical precipitation is tested for purification of acidic solution and it is found that the total loss of vanadium is 15.52%. commercial usage of this method is under study [15, 55, 80].

## 2.5. Precipitation

Precipitation is the final operation of vanadium processing and can be done in various ways [5]. Table 7 indicates several vanadium precipitation methods and compares them.

The pH value is a key parameter for the separation, and recovery of vanadium, which increases the pH value, and increases vanadium recovery. [20,73]. The low initial solution pH can prevent the hydrolysis of iron, aluminum, and the formation of silica compounds [73]. The simplest and long-used way to recover vanadium pentoxide is by adjusting the pH value to 2-3, using hydrolysis, and red cake precipitation [4]. This procedure is shown in Figure 7 [5].

Despite the variety of vanadate precipitation, the target product is always vanadium pentoxide [81]. Ammonium, calcium, and iron salt method can be used to precipitate vanadium pentoxide [18,81]. Depending on the value of pH, the precipitation by ammonium salts is divided into acid precipitation (at pH 2-3), weak acid precipitation (at pH 4-6), and alkaline precipitation (at pH 8-9) [81]. In this method, ammonium salts such as ammonium chloride ( $\text{NH}_4\text{Cl}$ ), and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) are widely used to precipitate vanadium pentoxide due to their high-grade products and easy operation [26,79]. Vanadium can be precipitated through this procedure as ammonium polyvanadate (APV,  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ ), also known as orange cake) or AMV ( $\text{NH}_4\text{VO}_3$ ) [4,18,26]. However, using ammonium salts for vanadium precipitation generates a high volume of ammonia wastewater, which is a threat to the environment [79, 82]. Figure 8 illustrates the precipitation of vanadate by the ammonium salt method under weak acid conditions [19].

In the calcium salt method, the precipitation of vanadium is based on the formation of calcium vanadate ( $\text{CaO} \cdot \text{V}_2\text{O}_5$ ) by using the calcium

Table 7. Comparison of vanadium precipitation by different methods.

Precipitation method	Sediment	Chemical formula	Precipitation pH	Vanadium solution concentration (g/L)	Acid consumption	Ammonium consumption	Precipitation temperature (°C)	Precipitation efficiency%	VZ05 purity%	Waste production	Reference
Precipitation of vanadate by hydrolysis vanadium (V)	Red cake, sodium hexapolyvanadate	$\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	1.5-3	5-8	Large	No	90	98	80-90	Effluent	[81]
Precipitation of vanadate by hydrolysis vanadium (IV)	Tetravalent vanadium acid	$\text{VO}_2 \cdot n\text{H}_2\text{O}$	3.5-7	20	Large	Minor	Room temperature	-	80-90	Effluent	[81]
Acidic precipitation of vanadate leaching solution by ammonium salt	Ammonium hexapolyvanadate	$2\text{NH}_3 \cdot 3\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	2-3	Low or high	Large	Minor	75-90	>98	>99	Effluent, waste gas	[81]
Weak acidic precipitation of vanadate leaching solution by ammonium salt	Ammonium decavanadate	$(\text{NH}_4)_{6-x} \cdot \text{Na}_x \cdot \text{V}_{10}\text{O}_{28} \cdot 10\text{H}_2\text{O}$	4-6	High	Minor	Large	Room temperature	>98	>99	Effluent, waste gas	[81]
Basic precipitation of vanadate leaching solution by ammonium salt	Ammonium metavanadate	$2\text{NH}_3 \cdot \text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$	8-9	High	Minor	Large	Room temperature	>98	>99	Effluent, waste gas	[81]
Use of calcium vanadate	Calcium pyrovanadate	$2\text{CaO} \cdot \text{V}_2\text{O}_5$	5-11	Low or high	-	-	Room temperature	97-99.5	Low	Effluent	[81]
Use of iron vanadate	Iron vanadate	$x\text{Fe}_2\text{O}_3 \cdot y\text{V}_2\text{O}_5 \cdot z\text{H}_2\text{O}$	<7	Low or high	-	-	Room temperature	99-100	Low	Effluent	[81]
membrane electrolysis	Sodium vanadate	$\text{NaHV}_6\text{O}_{16}$	1.81-13.7	High	No	No	Room temperature	-	92.6	No	[82]
	Ammonium polyvanadate	$(\text{NH}_4)_2\text{V}_6\text{O}_{16}$	2-4	High	No	Minor	Room temperature	92.9	99	No	[83]

salts (calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), calcium chloride ( $\text{CaCl}_2$ )) [18,81]. The calcium vanadate is an intermediate product and can be dissolved through acidic ( $\text{H}_2\text{SO}_4$ , hydrochloric acid ( $\text{HCl}$ )) and alkaline (sodium bicarbonate ( $\text{NaHCO}_3$ )) conditions for the production of red cake or AMV, respectively [18,81]. Figure 9 is shown vanadium precipitation by the calcium salt [18].

Recently, the clean method is proposed for high purity vanadium recovery by membrane electrolysis [82]. In this process, sodium vanadate ( $\text{NaHV}_6\text{O}_{16}$ ) can be precipitated by the migration of sodium ions to the cathode side (leaving vanadate ions on the anodic side) through the membrane and eventually decreasing pH due to water oxidation (producing hydrogen ions) [82].

### 3. Extraction of vanadium pentoxide from natural ores

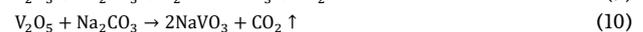
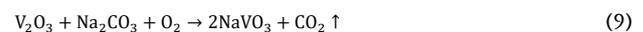
Vanadium pentoxide is extracted from the natural ores or concentrates of vanadinite, desclozite, and carnotite by salt roasting and leaching processes. During this process, the ore is first crushed and ground, then the obtained concentrate is mixed with a salt such as  $\text{Na}_2\text{CO}_3$ . The mixture is roasted and leached by dilute hydrochloric acid or sulfuric acid [84]. In addition, the vanadium can be leached out directly by sulfuric acid [84]. Figure 10 shows a flowsheet of vanadium pentoxide extraction from carnotite [84].

### 4. Extraction of vanadium pentoxide from titanomagnetite and iron ores

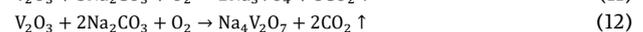
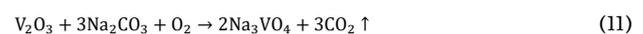
Vanadium can be recovered from titanomagnetite ore through hydrometallurgical treatment of salt-roasted titanomagnetite or pyrometallurgical processes. In the hydrometallurgical method, the vanadium compound is precipitated and recovered from the titanomagnetite ore/ concentrate leach liquor. However, in the pyrometallurgical method, vanadium slag is first prepared during the smelting of titanomagnetite ore and roasted. Then, a hydrometallurgical process (leaching, purification, and precipitation) is applied to it [4,24,85].

#### 4.1. Vanadium pentoxide extraction by direct extraction method

In This method, first, the titanomagnetite ore is dressed through crushing, milling, and magnetic separation stages, and the iron concentrate is obtained. Due to high vanadium content (above 1 wt%  $\text{V}_2\text{O}_5$ ), the sodium salt roasting-water leaching process is typically used for direct extraction of vanadium [15]. In this process, the materials are often mixed with sodium carbonate and roasted in the presence of oxygen in the temperature range of 900 to 1200°C by reaction (9) and reaction (10). With this process, sodium vanadate ( $\text{NaVO}_3$ ) compounds are formed, and the solubility of vanadium increases. Leaching temperature, the concentration of the leaching reagent, feed particle size, and the presence of impurities are influential factors in the leaching process [4].



If the roasting additive is added in excess, sodium orthovanadate ( $\text{Na}_3\text{VO}_4$ ) and sodium pyrovanadate ( $\text{Na}_4\text{V}_2\text{O}_7$ ) may be formed through reaction (11) and reaction (12). These compounds have less solubility than sodium metavanadate in water. In addition, the insufficient concentration of roasting additives will produce compounds called bronzes, which are insoluble in water [4].



After the roasting process, the materials are leached, and a vanadium-containing solution is formed. Neutral, cationic, and anionic species of vanadium vary depending on the values of Eh, pH, and concentration of vanadium [4, 18, 26]. According to Figure 11, at pH values above 10 to 12,  $\text{V}_2\text{O}_7^{4-}$  and  $\text{V}_3\text{O}_9^-$  polyvanadates, and in acidic medium,  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$  and  $\text{V}_{10}\text{O}_{28}^{6-}$  species are present in the solution.

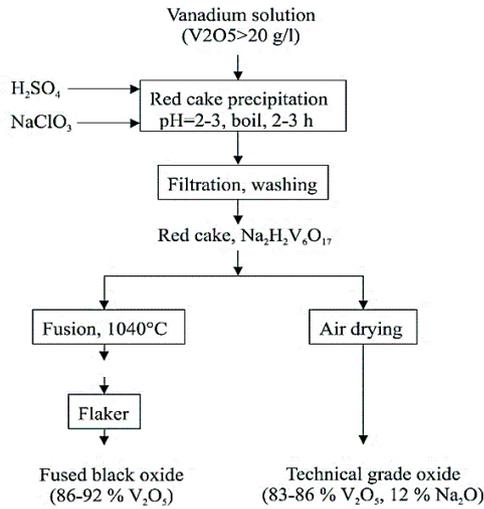


Figure 7. Vanadium extraction through red cake precipitation by hydrolysis method [5].

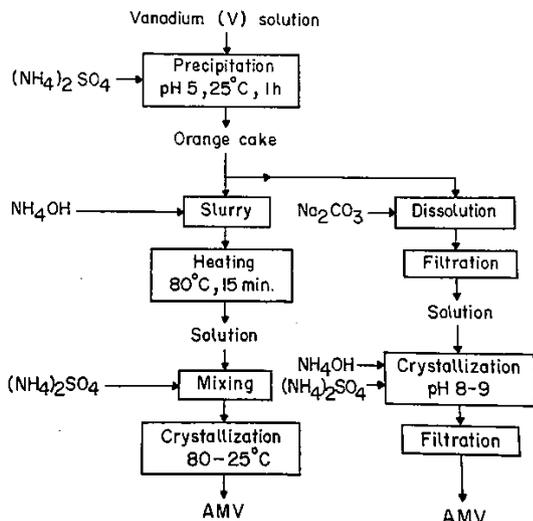


Figure 8. Vanadium precipitation by ammonium salt method [18].

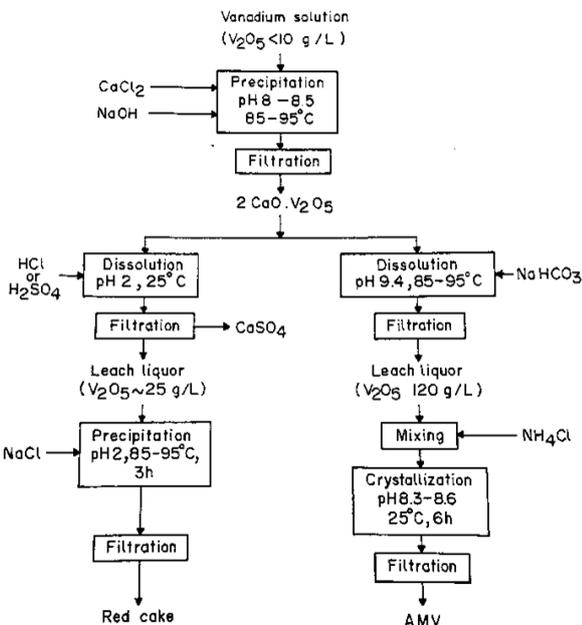


Figure 9. Vanadium precipitation by calcium salt method [18].

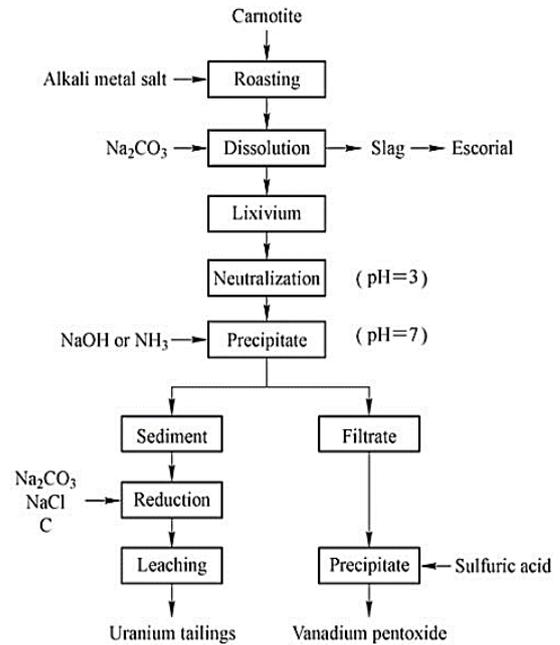


Figure 10. Flowsheet of vanadium extraction from carnotite [84].

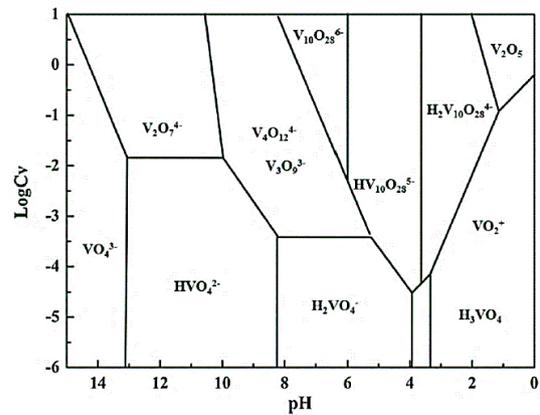
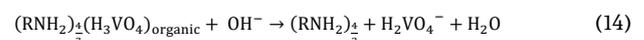
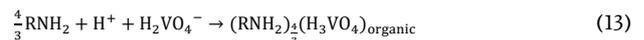


Figure 11. Diagram showing the relationship between the status of vanadium species in aqueous solution, pH, and vanadium concentration at 25°C [26].

At natural pH, sodium metavanadate reacts with water, and V(V) is formed as vanadium dihydrogen ( $H_2VO_4^-$ ) ions by reaction (10) [4,26].

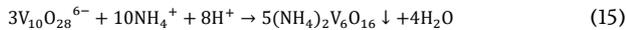
During the roasting process, silica will be dissolved in the leach liquor as soluble silicate compounds [4]. For silica impurity removal, aluminum sulfate ( $Al_2(SO_4)_3$ ) with flocculent are effective [4]. Aluminum sulfate and sulfuric acid are used in industrial operations [4,24].

For further purification of the vanadium solution, an amine-based cationic organic extractant such as N1923 can be used due to the negative ions formed through the reaction (5). After dihydrogen ions are loaded based on the reaction (13), the vanadium-loaded organic is stripped by ammonia or sodium hydroxide and the solution is purified by the reaction (14).



By adjusting the pH of leach liquor to 2, the ions in the acidic solution are hydrolyzed and aqueous vanadium pentoxide or red cake is precipitated with the combination of sodium hexavanadate ( $Na_2H_2V_6O_{17}$ ) [4,18,85]. The grade of vanadium pentoxide in red cake

is about 85%, and it contains many impurities [4,23,24,64]. By washing and melting this product, the melt is charged into the flake and flaked vanadium pentoxide is produced at 1040 °C [5,18]. In addition, vanadium can be precipitated and isolated as ammonium polyvanadate from leach liquor by adding ammonium salts through reaction (15) [26].



To produce a higher-grade product according to reactions (16) and (17), ammonium metavanadate should be precipitated by further processing of the red cake or ammonium polyvanadate, which is done by dissolving the red cake or ammonium polyvanadate in sodium carbonate solution and then adjusting the pH value to the range of 8 to 9 and adding ammonium sulfate [85]. In addition, this work is done directly in the alkaline solution to precipitate ammonium polyvanadate by using ammonium salts from the leached solution based on the reaction (18). In an acidic solution, the addition of ammonium salts causes the formation of ammonium hexamethylene ((NH<sub>4</sub>)<sub>2</sub>V<sub>6</sub>O<sub>16</sub>) which, can be prepared by calcining vanadium pentoxide powder. Then by calcining ammonium polyvanadate at 500 °C, according to the reaction (19), it is possible to produce a vanadium pentoxide product with a grade of 98 to 99.9% [24,26,86].

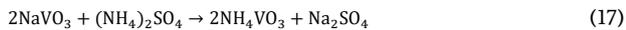
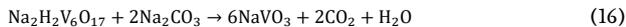


Figure 12 shows the general flowsheet for the extraction of vanadium pentoxide from titanomagnetite by direct extraction method (sodium roasting-water leaching) based on some industrial operations used at Windimurra in Australia [24], Rhovan, and Vantech in South Africa [24], and Otanmäki vanadium plants in Finland [4]. Based on the typical industrial indicators, vanadium pentoxide can be obtained with a purity of 99.5-99.8% by sodium roasting-water leaching. In this process, the vanadium leaching efficiency and the total recovery of the process are 97% and 74.41-78%, respectively [84].

Chen et al. applied hydrochloric acid as a leaching reagent and a mixture of D<sub>2</sub>EHPA and tri-butyl phosphate (TBP) solvent extractants for selective vanadium separation. This process has been able to produce vanadium pentoxide with a purity of 99.12% from the pre-reduced low-grade titanomagnetite [74]. In another report, Zhao et al. proposed the process of reduction-roasting and leaching with hydrochloric acid to recover vanadium [4]. In this process, first, the iron in titanomagnetite ore is reduced and then removed from the feed by magnetic separation. Then, the material is leached with hydrochloric acid, and vanadium pentoxide is precipitated from a vanadium-containing solution [4]. However, this method produces a large amount of acidic sewage that pollutes the environment [87]. Bian et al. proposed the ammonium chloride-acid leaching-solvent extraction, which was carried out to separate vanadium, titanium, and iron from vanadium-bearing titanomagnetite. The extraction rates of vanadium, titanium, and iron reached 95.1%, 1.2%, and 92.5%, respectively [88].

In a study, Mahdilou et al. investigated the extraction of vanadium from titanomagnetite ore; it has been found that the parameters of roasting additive concentration, temperature, feed particle size, and time in the roasting process and temperature, time, and feed particle size parameters are effective in the leaching process [23].

Tabatabai et al. have obtained a vanadium-rich solution with more than 80% recovery by applying the sodium roasting-leaching process on Choghart iron ore [51]. Some variables such as temperature, time of leaching, feed granulation, and concentration of leaching reagent have been reported as effective parameters [51].

#### 4.2. Vanadium pentoxide extraction from co-product slag by smelting method

In the pyrometallurgical method, the vanadium-containing iron concentrate is smelted, and by blowing oxygen into the molten pig iron, a vanadium-rich slag is produced. Then, the hydrometallurgical process is performed on the obtained slag [4,89].

To obtain molten pig iron and extract valuable titanomagnetite elements, blast furnace-converter or direct reduction-arc furnace processes are used [87]. In the blast furnace process, titanomagnetite concentrate is smelted in the blast furnace to obtain molten pig iron and blast furnace slag. During this operation, metallic titanium enters the slag in the form of titanium dioxide (TiO<sub>2</sub>), which contains approximately 22 to 30% TiO<sub>2</sub> [88]. Molten pig iron contains about 0.5% vanadium. Then, vanadium is selectively oxidized from molten pig iron in the converter using oxygen blowing, and vanadium-rich slag is obtained, which contains about 14 wt.% of vanadium [24,43,87]. Figure 13 shows the blast furnace process at Chengde in China [24]. At present, in China, the blast furnace process is a very common method for smelting titanomagnetite [16]. However, the use of blast furnaces is not suitable for these ores. Viscous slag is formed due to the formation of titanium carbide or nitride, which causes the loss of valuable elements [4,87]. In addition, the relatively long cycle of production and the high energy consumption are other problems of this method [88].

Reduction-arc furnace process is another pyrometallurgical process for the extraction of vanadium from the titanomagnetite sources. The vanadium-bearing iron concentrate obtained from the beneficiation of titanomagnetite is reduced in a rotary kiln with coal. Then, the reduced materials are charged into an electric arc furnace. Smelting materials in the furnace obtain molten pig iron and slag. Slag contains a high amount of titanium and a small amount of vanadium. The molten pig iron is transferred to the converter or shaking ladles and by blowing oxygen, vanadium-rich slag is obtained. This process is used in the Highveld steel plant to produce vanadium slag, which contains about 24% vanadium pentoxide [24]. The Highveld process is shown in Figure 14 [5]. Finally, to produce a high-purity vanadium pentoxide, the slag is roasted and leached. By the purification of the leach liquor, vanadium pentoxide is precipitated using ammonium salts. Unlike roasted titanomagnetite ore/concentrate, the particle size of roasted slag has a poor effect on vanadium extraction and lower temperatures are required to form vanadium-soluble compounds [4]. However, in a study conducted by Mahdavian et al. on the slag of the Mobarakeh Steel Converter, the particle size of slag has a significant effect on vanadium recovery [90]. Table 8 presents a comparison of vanadium extraction obtained from the research works for vanadium-bearing ores, concentrates, and slags.

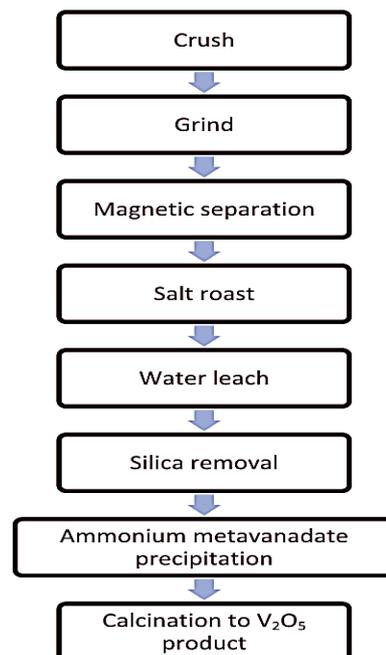


Figure 12. General flowsheet of vanadium extraction from titanomagnetite ore by direct extraction process [4]

**Table 8.** Comparison of vanadium extraction from the vanadium-bearing ore/concentrate and steel slag based on research works.

Vanadium resource	Vanadium concentration (V)	Method	Optimum conditions										Vanadium recovery	Ref.
			Roasting			Leaching				Liquid to solid ratio				
			Temperature	Time	Salt content	reagent	Acid or base concentration	Time	Temp					
Steel converter slag	1.2%	Sodium roasting-acid leaching	1000 °C	2 hours	20 wt.% Na <sub>2</sub> CO <sub>3</sub>	Sulfuric acid	3 mol/L	150 min	70 °C	15	>95%	[91]		
Vanadium-bearing iron ore	0.8%	Sodium roasting-water leaching	1100 °C	3 hours	13 wt.% Na <sub>2</sub> CO <sub>3</sub>	Water	-	3 hours	90 °C	-	>80%	[91]		
Vanadium-bearing iron ore	0.35%	Sodium roasting-acid leaching	1010 °C	2.1 hours	41 wt.% Na <sub>2</sub> CO <sub>3</sub>	Sulfuric acid	4.25 mol/L	4.7 hours	85 °C	12.4	>83%	[91]		
Vanadium-bearing ore	0.2%	Sodium roasting-acid leaching	1000 °C	1 hour	50 wt.% Na <sub>2</sub> CO <sub>3</sub>	Sulfuric acid	15 v/v% (Volume per volume)	4 hours	90 °C	15	80%	[91]		
Vanadium-bearing titanomagnetite concentrate	0.48%	Sodium roasting-water leaching	1100 °C	2 hours	16 wt.% Na <sub>2</sub> CO <sub>3</sub>	Water	-	1 hour	90 °C	4	>80%	[91]		
Cr-V slag	-	Sodium roasting-water leaching	800 °C	2 hours	-	Water	-	1 hour	25 °C	3	>87%	[91]		
Steel converter slag	0.95%	Sodium roasting-alkali leaching	1000 °C	45 min	10 wt.%	Na <sub>2</sub> CO <sub>3</sub> and NaOH	Na <sub>2</sub> CO <sub>3</sub> : 40-50 g/L NaOH: 10 g/L	60 min	80 °C	15	>80%	[91]		
Cr-V slag	5.16%	Sodium roasting-water leaching	850 °C	90 min	15 wt.% NaOH, 35 wt.% Na <sub>2</sub> CO <sub>3</sub>	Water	-	30min	90 °C	3	>95%	[91]		
Steel converter slag	1.2%	Sodium roasting-acid leaching	1000 °C	2 hours	20 wt.% Na <sub>2</sub> CO <sub>3</sub>	Sulfuric acid	2.05 mol/L	60 min	70 °C	19.99	>96%	[91]		
Vanadium slag	4.73%	Sodium roasting-alkali leaching	850 °C	60 min	10 wt.%	Sodium carbonate	160 g/L	150 min	95 °C	10	>90%	[91]		
Steel converter slag	3.5%	Sodium roasting-water leaching	850 °C	60 min	50 wt.%	Water	-	-	-	-	>85%	[91]		
Cr-V slag	-	Calcium roasting two-step acid leaching	800 °C	1 hour	12.3 wt.% Na <sub>2</sub> CO <sub>3</sub>	Sulfuric acid	-	Step 1: 20 min Step 2: 20 min	Step 1: 50 °C Step 2: 50 °C	Step 1: 10 Step 2: 5	>87%	[91]		
Titanomagnetite concentrate	-	Sodium roasting-water leaching	1150 °C	-	6-8 wt.% sodium salt	Water	-	-	90 °C	-	>75%	[15]		

Approximately 60% of global vanadium products are obtained using the traditional sodium salt roasting process [81]. Although the most problems such as the low vanadium conversion rate of single roasting (about 65-85%) [58], agglomeration of slag melting at high roasting converter slag is the sodium roasting-water leaching process, it has some mature and economical technology for extracting vanadium (from the

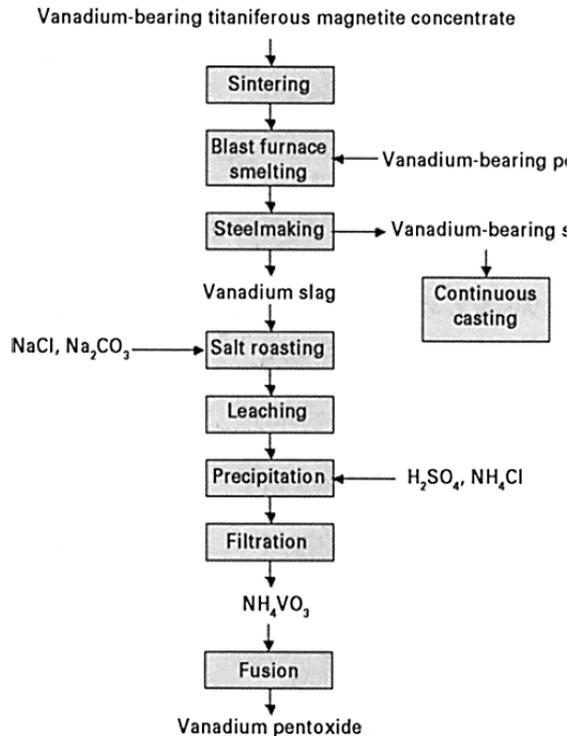


Figure 13. Vanadium extraction by blast furnace in China [24].

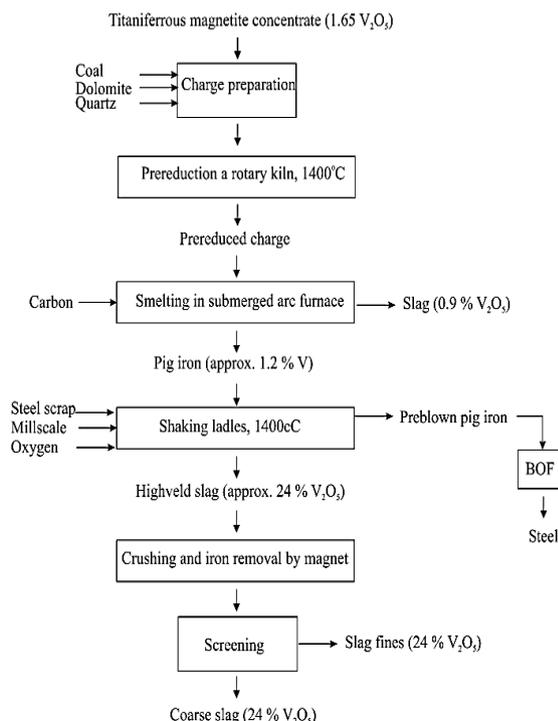


Figure 14. Flowsheet of vanadium-rich slag production by Highveld process [5]

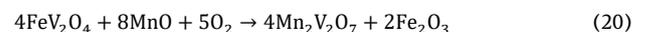
and chlorine ( $\text{Cl}_2$ ), discharge of large volumes of vanadium wastewater (approximately 30,000 to 50,000 kg of wastewater per 1000 kg of vanadium pentoxide) [61]. In addition, it causes problems in the use and disposal of waste [26,63] and high energy consumption in multiple roasting for a more vanadium conversion rate [58]. Therefore, calcium roasting as a clean technology is an alternative to sodium roasting [26] where limestone or other calcium-containing compounds are used [26]. It is usually combined with acidic leaching [91]. Also, a new method has been introduced, in which no salt is used in the Cr-V slag (a slag with high chromium content) roasting. Non-salt roasting prevents the production of carcinogenic compounds of chromium under sodium and calcium roasting [26,61].

#### 4.3. Proposed and novel methods for vanadium extraction from titanomagnetite

Based on previous discussions, using the sodium roasting-water leaching process to extract vanadium from steel converter slag has some disadvantages. Several processes have been proposed as alternatives, such as direct acid leaching, non-salt roasting-ammonium leaching, and calcium roasting-acid leaching [92]. In addition, in recent years, methods such as multistage recovery and sub-molten salt (SMS) have been developed [92]. However, the high cost and procedure operational complexity prevent their industrial applications [92].

In vanadium slag (Specially Cr-V slag), Chromium spinel ( $\text{FeCr}_2\text{O}_4$ ) can be oxidized and converted to toxic hexavalent chromium under alkaline roasting conditions and generate hazardous waste that is treated environment [26]. Therefore, recently, the non-salt roasting-ammonium leaching process was introduced by Du and applied converter slag to eliminate the problems of sodium roasting-water leaching procedure, remove the hazardous hexavalent chromium waste (Carcinogenic to humans, classified in Group 1 by the International Agency for Research on Cancer (IARC)) and production of saleable leach residue, that can be used in the iron industry [26,33]. In addition, in recent years, calcium roasting-acid leaching has attracted attention and many studies have been done on it. This process has good potential for cleaner production, less water consumption, and less wastewater production. Also, corrosive gases are not formed in calcium roasting [16]. However, this process has several disadvantages such as the precipitation of calcium sulfate layer on solid particles and reduction of leaching rate, the reaction of single vanadium spinel with calcium and the need for mechanical activation to prevent it [64], difficulty of purifying vanadium acidic solution due to the emulsion, third phases phenomena that cause loss of vanadium and poisoning ion exchange resin, and producing lower grade product than the sodium roasting process due to the increase of impurities such as manganese and phosphorus [26,80,92], operation difficulty, low recovery of vanadium and problem to use leach residue in the iron industry [61].

Lee et al. applied the non-salt roasting- ammonium leaching process on a slag with 10.65 wt.% vanadium pentoxide to study the parameters affecting the process and develop new approaches, that would help to produce vanadium pentoxide cleanly from slag [61]. In this study, shown in Figure 15, vanadium slag was roasted for 2 hours at 900 °C, and then leached in ammonium bicarbonate solution. According to X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDXS) analysis; it was found that the phases consisting of V(V) are manganese vanadium oxide ( $\text{Mg}_2\text{V}_2\text{O}_7$ ), and magnesium vanadium oxide ( $\text{Mn}_2\text{V}_2\text{O}_7$ ). These phases are formed over time during the roasting process when the slag resources (magnesium and manganese oxide) react with vanadium spinel in the presence of oxygen. Then, vanadium spinel ( $\text{FeV}_2\text{O}_4$ ) disappears and hematite is formed by reaction (20) [61]. It is found that as the roasting temperature arose, the minority of  $\text{Cr}^{3+}$  ions in the spinel phase can be combined with  $\text{VO}_2$  and formed the  $\text{Cr}_{0.07}\text{V}_{1.93}\text{O}_4$  or  $\text{CrVO}_4$  compounds [26].



In the next step, magnesium vanadium oxide is leached with ammonium bicarbonate solution and AMV is formed based on the reaction (21).

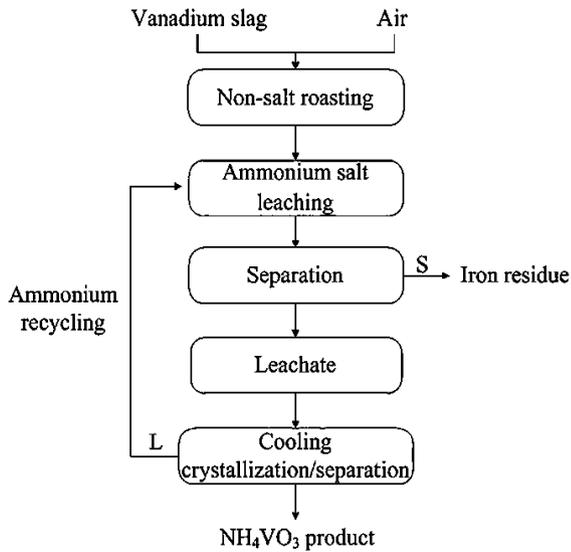
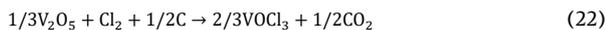


Figure 15. Flowsheet of the non-salt roasting-ammonium leaching process [61].



In addition, it was found in this process that keeping the other parameters constant, reducing the slag particle size, concentration of leaching reagent and leaching temperature have a significant effect on leaching rates. However, there are impurities in the leached solution that require more work to remove and produce higher-quality vanadium pentoxide powder [61].

Figure 16 shows a new process, which has recently been proposed for the cleaner extraction of vanadium pentoxide from slag [93]. The principles of this process are similar to the chloride method for the commercial production of titanium dioxide. Vanadium, like titanium, can be extracted through this method by combining the vanadium-containing materials with chlorine ( $\text{Cl}_2$ ) to produce vanadium oxytrichloride ( $\text{VOCl}_3$ ) by reaction (22) [93].



In this process, chlorination temperature is a key parameter [93]. About 95% of vanadium can be extracted at 850 °C [93]. After separation and purification, vanadium pentoxide is produced by the reaction of vanadium oxytrichloride with oxygen [93].

The advantages of the chlorination method are the generation of a swage with low ammonium content, an excellent distillation of vanadium oxytrichloride, having a suitable residue for the iron industry, and guaranteeing the production of vanadium pentoxide with high purity (99.99%). However, impurities such as iron increase chlorine consumption and must be separated [93]. Additionally, this process has disadvantages such as toxic and corrosive chlorine environmental pollution, requiring anticorrosive equipment, high reaction temperature, and energy consumption [94]. Du et al. have applied the chloride method to vanadium slag with petroleum coke, which has been shown to disintegrate the vanadium spinel structure and produce vanadates and iron-rich oxides, leading to selective vanadium chlorination [93].

Anhydrous aluminum chloride ( $\text{AlCl}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ), solid ferric chloride ( $\text{FeCl}_3$ ), and ferrous chloride ( $\text{FeCl}_2$ ), instead of chlorine have been investigated for the production of vanadium oxytrichloride [94-96]. The magnesian roasting-acid leaching method is proposed to extract vanadium from the vanadium slag shown in Figure 17 [16]. This process uses magnesium oxide ( $\text{MgO}$ ) as the roasting additive which in the next steps with multi-cycling, recovers the resources in the slag and non-harmful waste is produced. In addition, the roasting additive can be recycled and the cost of roasting is lower than other process additives [16].

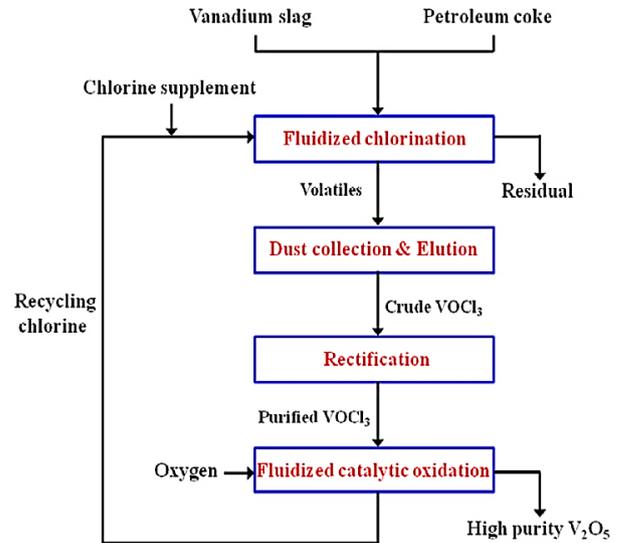


Figure 16. Flowsheet of chlorination process for extraction of vanadium from the vanadium slag [93]

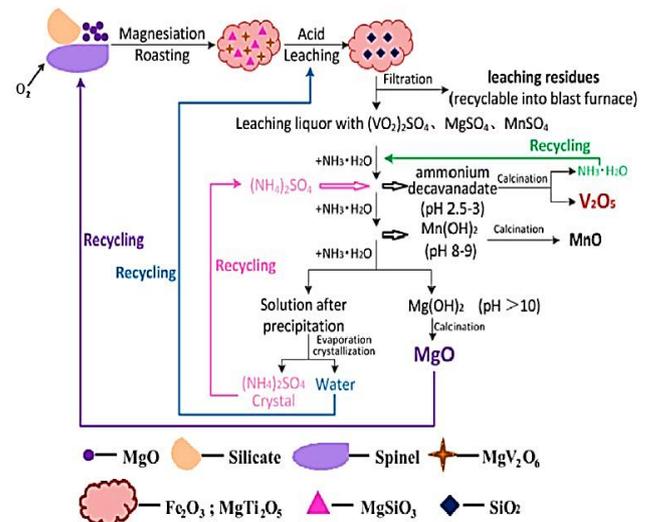


Figure 17. The flowsheet of magnesian roasting-acid leaching with multiple recycling [16]

Another process for extracting vanadium from slags is the SMS method [4]. This method uses the NaOH medium (approximately 50 w/w%), the KOH medium, and the NaOH-NaNO<sub>3</sub> media in the presence of oxygen, air, or nitrate to treat vanadium slag [58]. The rapid conversion rate of vanadium oxide is possible in molten NaOH, which melts at 323 °C. 80% NaOH can extract more than 90% vanadium at 210 °C [4]. Therefore, in the SMS technology (Figure 18), vanadium spinel required a low temperature (200-400 °C) to convert. No harmful gases are formed during the treatment, which makes it attractive for industrial applications [16,58]. In addition, up to 95%, vanadium and 90% chromium can be extracted. In the NaOH medium, only vanadium can be extracted from slag, but, in the KOH and the NaOH-NaNO<sub>3</sub> media, both vanadium and chromium can be extracted, which can be separated by water leaching, filtration, and crystallization processes [58]. However, there is no direct solvent extraction or ion exchange purification method to separate V(V) from the other impurities of leach liquor. Also, due to the high alkalinity of the solution, the purification process is acid-consuming [80].

Additionally, Chen et al. have investigated anhydrous sodium hydroxide roasting on the rich titanium-vanadium slag [58]. In this

developed method, rich titanium-vanadium slag is first obtained by carbon reduction, magnetite separation, and desilication. Then, the slag is roasted with sodium hydroxide salt at 500 °C. The decomposed material is leached with water and soluble sodium vanadate is leached out, but sodium titanate is remained solid. More than 96% of the vanadium is leached out by optimal conditions of leaching temperature of 50 °C, leaching time of 20 min, L/s ratio of 5:1, and sample size <104 microns. The vanadium-containing liquid is used to prepare high-purity vanadium pentoxide powder, and after impurity removal and crystallization, sodium hydroxide is recycled. Then, the washed solid is dissolved in sulfuric acid solution and titanium dioxide powder is obtained by purification of the titanyl sulfate ( $\text{TiO}(\text{SO}_4)$ ) solution, precipitation of titanic acid ( $\text{H}_2\text{TiO}_3$ ) [59]. Figure 19 presents the sodium hydroxide molten salt process [59].

## 5. Extraction of vanadium pentoxide from stone coal

The principles of vanadium recovery from stone coal include the oxidation of V(III) to V(IV) or V(V) compounds, which is followed by the roasting, leaching, solution purification, and precipitation of vanadium pentoxide [12]. Figure 20 shows the general methods for vanadium extraction from stone coal [15]. Processes such as calcium

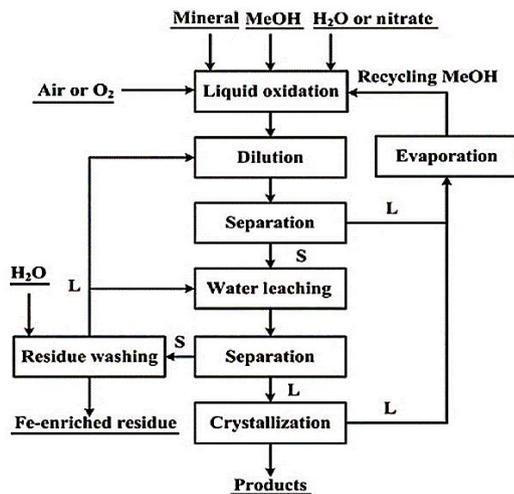


Figure 18. Simplified flowsheet of SMS process [58]

roasting-acid/alkali leaching [97], high salt roasting-water leaching (HSRWL), blank roasting-acid/alkali leaching (BRAL), barium salt roasting-acid leaching, and direct acid leaching (DAL) have been applied to extract vanadium from stone coal [12,15]. Different research works on vanadium extraction processes from stone coal have been presented in Table 9.

Wang et al. applied a calcium roasting- acid leaching process to the stone coal containing 0.28% vanadium pentoxide, in the best conditions, with roasting at 950°C for 4 hours, the sulfuric acid concentration of 40%, and 6 hours leaching, vanadium extraction rate has been 85.5% [97]. In this study, it has been found that the roasting temperature has a great effect on the extraction rate [97]. In the HSRWL technique, first, stone coal is decarbonized. Then, milled with sodium chloride and roasted at about 800 °C for 2 hours. In the next step, the roasted stone coal is leached with water. By adjusting the conditions, AMV is precipitated [12]. However, the sodium salt roasting process suffers from a low vanadium extraction rate (usually <50%) and severe environmental pollution [15]. In the BRAL technique, no salt is used in the roasting, and the vanadium pentoxide is obtained by leaching the roasted stone coal with sulfuric acid, purification of the solution, and precipitation of AMV. The blank roasting-dilute sulfuric acid and the direct leaching with concentrated sulfuric acid processes are used commercially. However, only stone coals with special character can be treated [56]. The leaching efficiency of vanadium in the blank roasting-

NaOH leaching and calcium roasting-sulfuric acid leaching is high. However, these processes suffer from the slow reaction rate of stone coal calcification and a narrow range of roasting temperature (900-950°C) [15,56]. In China, another industrial process is Barium salt roasting-acid leaching. The stone coal is mixed with barium carbonate ( $\text{BaCO}_3$ ) and roasted at 800-850°C. Then, dilute sulfuric acid is used to leach the roasted material [15]. In this process, the recovery of vanadium is relatively high (71%). However, the cost of barium salt is higher than sodium salts [15]. All of the aforementioned methods have disadvantages and there are many challenges in treating stone coal efficiently. Thus, the development of a green method with high efficiency deserves further attention [15,56].

Many studies have been done to recover vanadium from an aqueous solution by solvent extraction method. The chemical precipitation method can be removed impurities from the leach liquor obtained by the traditional sodium roasting-water leaching process. But many impurities are leached in acid leaching of the stone coal and the solvent extraction method has been used to treat leach liquor [80]. The most common study is the use of D2EHPA and TBP [98-101]. Le et al. compared the process of solvent extraction and ion exchange in the recovery of vanadium from the leach liquor of stone coal. In this study, ion exchange resins have been shown to have poor performance for the adsorption of V(IV) from solution. When the amount of Fe(III) increases, the adsorption of the resin decreases and even maybe blocked [102]. D2EHPA and EHEHPA extractants are commonly used to extract V(IV), and amines such as Aliquate 33 and Alamine 336 are used to extract V(V) from acidic solutions [65,102].

Lee et al. examined the extraction of vanadium from stone coal by using the acid leaching method under pressure; It was found that high-purity vanadium pentoxide powder is produced under pressure at 150°C and using TBP and P204 from solvent extraction synergism. The advantages of this method include short leaching time compared to conventional acid leaching methods and high vanadium recovery [103].

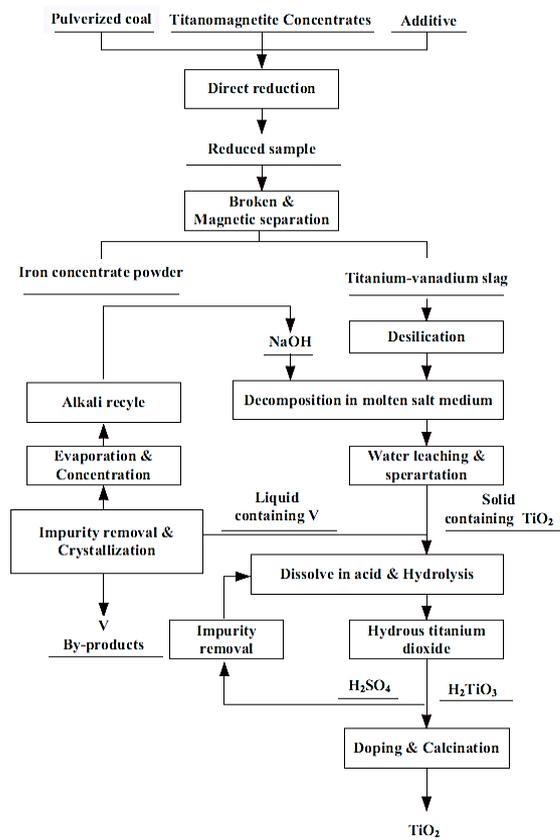


Figure 19. Flowsheet of sodium hydroxide molten salt process for extraction of vanadium, titanium, and iron from the titanomagnetite concentrate [59]

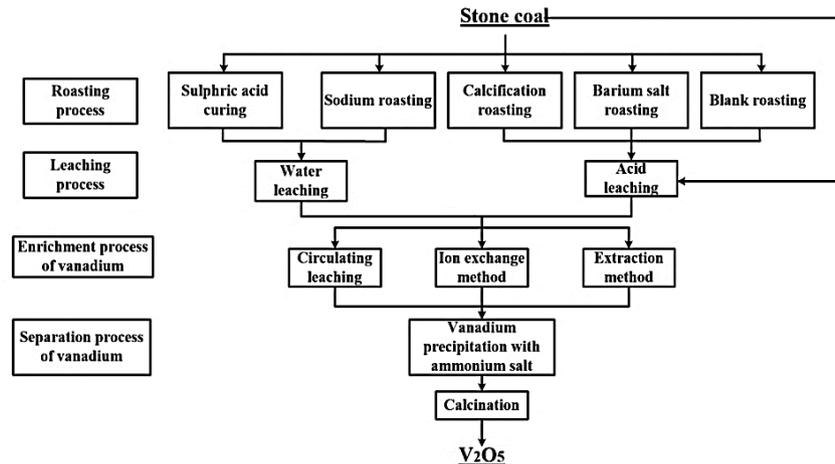


Figure 20. General strategies for vanadium extraction from stone coal [15].

Table 9. Comparison of Typical methods for vanadium extraction from the stone coal.

Extraction method	Grade of stone coal V <sub>2</sub> O <sub>5</sub> %	Roasting conversion efficiency%	Leaching efficiency%	Product grade V <sub>2</sub> O <sub>5</sub> %	Total recovery%	Ref.
High salt roasting- water leaching	>1	55	90	>98	45	[104]
Barium salt roasting-dilute sulfuric acid leaching	-	-	-	-	71	[15]
Direct sulfuric acid leaching	-	-	-	-	65-71	[104,15]
Direct sulfuric acid leaching with leaching helper reagent (fluorosilicic acid)	-	-	80	-	-	[104]
Blank roasting-sulfuric acid leaching	-	-	40-68	-	55-60	[15]
Calcification roasting-sulfuric acid leaching	-	87.6	85	99.5	65	[104]
Calcification roasting-sodium carbonate leaching	-	100	71.97	99.32	71.1	[104]

## 6. Extraction of vanadium pentoxide from industrial wastes

The presence of vanadium element in industrial wastes such as fly ash from oil burning and waste of the hydrometallurgical process (Bayer process) for the production of alumina is not hidden from anyone. In addition, a certain amount of vanadium is discharged into the environment as a large amount of vanadium wastewater and leaching residues (containing about 0.7-1.9% of the vanadium in calcium roasting- acid leaching with low recovery) during slag/ ore treatment, which requires serious attention due to environmental problems [105,106]. In industrial regions, significant amounts of waste are accumulated. Vanadium and its compounds have toxic effects on the environment. Thus, vanadium as a high-demand valuable element can be extracted from toxic vanadium-containing wastes in terms of environmental protection [107].

### 6.1. Vanadium extraction from oil-burning residues

Power stations used vanadium-containing oil as fuel and produced two types of waste ashes [19]. Usually, less amount of the oil ashes in the flame zone, deposited in furnace pipes or boiler tubes are called boiler ash (4.4-19.2% V) [18]. A large amount of the other ashes is collected by an ash collection system (cyclone collector or electrostatic precipitator) as fly ash than contains typically 3% V<sub>2</sub>O<sub>5</sub> [18,108,109]. Also, a trace amount of vanadium can exist in Bituminous coal. The Typical fly ash from the burning of coal contains 11.7 wt.% V [84]. The acid/ alkaline leaching, alkali treatment (sodium carbonate roasting and water leaching), and pyrogenic (vanadium slag production by Smelting the mixture of oil residue and Sodium salts (Na<sub>2</sub>CO<sub>3</sub> or NaCl) in the presence of sulfate or sulfide) and direct pressurized leaching processes are used to extract vanadium from the vanadium-containing oil residues [84]. In addition, ashes with high carbon content can be treated with a carbon oxidation (decarburation) process followed by the sodium salt

roasting-water/alkali leaching [84]. The Petrofina process has been used for the commercial extraction of vanadium pentoxide from fly ash on a large scale. In this process, vanadium-containing fly ash was leached by direct acid leaching under pressure in the extraction vessel, and pure vanadium pentoxide precipitated from the leach liquor [18]. Another developed commercial method is the Sotex process. The reduction of vanadium to tetravalent form (V(IV)), leaching with sulfuric acid and solvent extraction processes were used for vanadium precipitation as VO<sub>2</sub>.nH<sub>2</sub>O and Acid red (HVO<sub>3</sub>) cake in the Sotex method [18]. The properties of Petrofina, Sotex, and other processes have been presented in Table 10.

High energy consumption and metal loss are disadvantages of the pyrometallurgical process for the treatment of vanadium-containing industrial wastes such as fly ash and spent catalyst [110]. Therefore, in the extraction of vanadium from fly ash, hydrometallurgical processes are usually preferred [110], which use the roasting and solvent extraction processes to recover vanadium [32]. Figure 21 shows a typical process for treating fly ash [84].

It should be noted ash roasting, have a positive or negative effect on vanadium extraction [65]. Acid, water, or base can be used in the ash-leaching process [32]. It also has been found; that temperature is the most effective parameter in the leaching of ash with sulfuric acid [111]. Acidic reagents introduce various impurities into the solution in significant amounts that make it difficult to purify the solution. However, the use of alkaline reagents for more selective dissolution of vanadium is more appropriate but less effective [65]. The Aliquot 336 is considered the best solvent extractant due to its higher efficiency. In addition, the process of selective precipitation due to the removal of interfering metals such as aluminum, which causes problems in the stripping of the organic solution, is introduced after alkaline leaching [65].

Table 10. Comparison of different processes for vanadium extraction from oil residues.

Extraction method	Conditions	Source	Grade of oil residue V%	Roasting conversion efficiency%	Leaching efficiency%	Product grade V <sub>2</sub> O <sub>5</sub> %	Precipitation efficiency%	Total recovery%	Ref.
salt roasting- alkali leaching- solvent extraction	<b>Leaching:</b> Reagent: NaOH (8 M) Temperature: 112 °C Time: 4 h	Boiler ash	4.4-19.2	-	Stage 1: 43 Stage 2: 16 Stage 3: 43	-	-	80	[84]
	<b>Solvent extraction:</b> Extraction: 25% LiX, 64N, pH 6 Reverse extraction (stripping): HCl (6 M)								
Decarburization- sodium roasting- water/alkali leaching	<b>Roasting:</b> Temperature: 850 °C	Boiler ash	-	-	99	-	89	83	[84]
Direct acid leaching under pressure	<b>Leaching:</b> Reagent: acid (60 g/L) Pressure: 1.5 MPa Temperature: 200 °C Liquid-solid ratio: 1:1	Boiler ash	-	-	>95	-	-	-	[84]
Alkali leaching	<b>Leaching:</b> Reagent: ammonia (NH <sub>3</sub> ) (0.25 M) and (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1M)	Fly ash	0.41	-	60	-	-	-	[84]
Alkali leaching	<b>Leaching:</b> NaOH	Fly ash	0.41	-	80	-	-	-	[84]
Direct acid leaching under pressure (Petrofina process)	<b>Leaching:</b> Reagent: Sulfuric acid Pressure: 300 KPa	Fly ash	-8.4	-	-95	99	-	90	[18]
Reduction- acid leaching- solvent extraction (Sotex process)	<b>Leaching:</b> Reagent: Sulfuric acid, Temperature: 50-100 °C,	Soot and ash	-	-	-	-	-	-	[18]
	<b>Solvent extraction:</b> Extraction: 20% D2EHPA and 15% TBP Reverse extraction (stripping): H <sub>2</sub> SO <sub>4</sub> (1.5 M)								
Alkali leaching	<b>Leaching:</b> Reagent: Na <sub>2</sub> CO <sub>3</sub> (1.3%) Temperature: 100 °C Time: 24 h	Fly ash	-19.8	-	-90	-	-	-	[18]
Direct alkali leaching	<b>Leaching:</b> Reagent: NaOH (1.3%) Temperature: 100 °C Time: 12 h	Fly ash	-19.8	-	97.7	-	-	-	[18]
Decarburization- vapor sodium roasting-alkali leaching	<b>Roasting:</b> Reagent: NaCl Temperature: 750 °C Salt-ash ratio: 1:6	Fly ash (containing 40% carbon)	-	-	86.5	-	-	-	[18]
	<b>Leaching</b> Reagent: NaOH (2N) Temperature: 110 °C								
Decarburization- vapor sodium roasting-alkali leaching	<b>Roasting:</b> Reagent: NaCl Temperature: 750 °C Salt-ash ratio: 1:12	Fly ash (containing 40% carbon)	-	-	70	-	-	-	[18]
	<b>Leaching</b> Reagent: H <sub>2</sub> SO <sub>4</sub> (2N)								

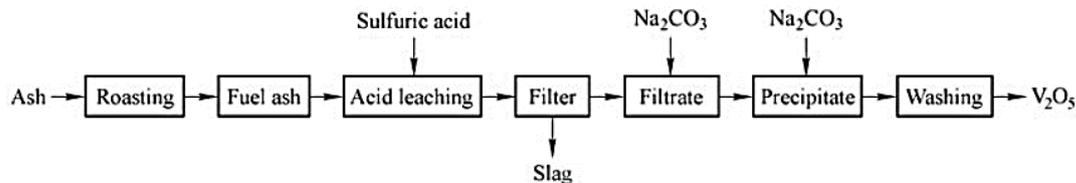


Figure 21. The typical process to treat fly ash for extraction of vanadium [84].

Nazari et al. used a combustion step to reduce the carbonated part of the ash to extract vanadium, which has the advantage of reducing the volume of residue compared to the direct ash sales method. Unfortunately, there is no fixed process for the direct recovery of vanadium from ash [111].

### 6.2. Vanadium extraction from red mud

Red mud or Bayer sludge, a waste generated during the production of alumina from bauxite ores, contains valuable elements such as vanadium. The carbon adsorption and desorption method have been proposed to recover vanadium from red mud. In this process, the red mud is first leached in hot water for half an hour, then vanadium is adsorbed on carbon by adjusting the pH value to 2.5 and temperature to 80 °C. In the next step, the charged activated carbon is desorbed with an ammonia solution at 85 °C. With this process, vanadium pentoxide with a purity of 99.9% is obtained [20]. This process is shown in Figure 22 [18]. In the separation of vanadium from the leach liquor of red mud with resins, anionic resin, D201 had the highest load of this element [23].

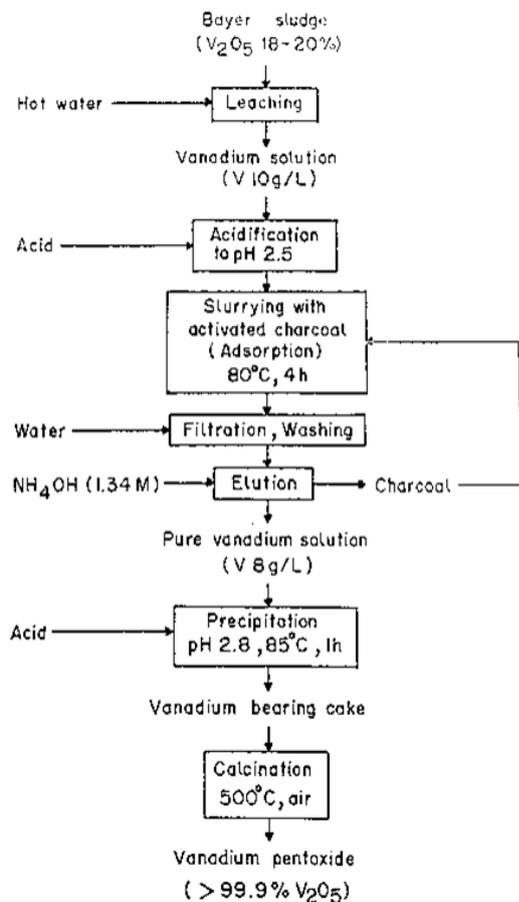


Figure 22. Carbon adsorption and desorption process to prepare vanadium pentoxide from Bayer sludge (red mud) [18].

### 6.3. Vanadium extraction from spent catalysts

In the manufacture of sulfuric acid, vanadium catalysts such as  $V_2O_5$ ,  $NH_4VO_3$  is mainly used to convert  $SO_2$  to  $SO_3$  [84]. In addition, vanadium is widely used as a  $VCl_4$  catalyst in the rubber industry and as the VS catalyst for pyrolysis and desulfurization in the petroleum refining industry [84]. Large quantities of vanadium-containing catalyst wastes are generated from the hydrotreating process for refining purposes such as Hydrodesulfurization (HDS) catalysts [112]. The various hydrometallurgical processes are developed for vanadium extraction from spent crude oil HDS catalyst which contains 1-12% vanadium. These processes include leaching, solvent extraction, and precipitation. On the other hand, the pyrometallurgical process (the vanadium is mainly trivalent) like roasting has been used in combination with the hydrometallurgical process [42,112]. Besides vanadium, other valuable metals (such as molybdenum (Mo), cobalt (Co), and nickel (Ni)) can be recovered during the treatment of spent petroleum catalysts [18]. The direct leaching of spent catalyst is performed at high pressures or high temperatures [42]. The inorganic acids such as  $H_2SO_4$ ,  $HNO_3$ ,  $HF$ ,  $HClO_4$ , organic acids like oxalic, citric acid, and alkalis such as  $NaOH$ ,  $Na_2CO_3$ ,  $NH_3$  are used as leaching reagents in acid and alkali leaching, respectively [112]. Table 11 presents different processes for vanadium extraction from the spent catalysts. The Sodium carbonate roasting-water leaching process (Figure 23) is the only industrial method for treating spent Hydrodesulfurization catalysts [112]. It can be recovered 90-95 wt.% and selectively extracted vanadium and molybdenum over cobalt, nickel, and aluminum [42,112].

Mohanty et al. investigated the sodium roasting-water leaching from a typically spent catalyst with approximately 2.5%  $V_2O_5$ . In this study, the sample is first roasted with 50 wt.%  $Na_2CO_3$  at 700°C for 30 min, and leached by water with the pulp density of 1:6 solid/liquid at room temperature for 15 min. under these optimum conditions, the recovery of vanadium reached about 80%. The final product is heated at 650°C to obtain 92.6% vanadium pentoxide. In addition, the recovery of the vanadium increased to above 99% when sodium sulfite ( $Na_2SO_3$ ) added to water during leaching [112].

In another study, Khorfan et al. obtained vanadium pentoxide powder from a spent catalyst that contains 5.5%  $V_2O_5$  by acid leaching, oxidation, and precipitation process. The sample is first grounded and leached by sulfuric acid. Under the optimum conditions; phase ratio (S/L): 1/5 g/ml, acid concentration:15% v/v, mixing time: 1 hour, leaching temperature: 100°C, 96.6% of vanadium is leached out to the solution. Then, hydrogen peroxide ( $H_2O_2$ ) with a concentration of 15% is added to the solution to oxidize vanadium to vanadium pentoxide. The final product is precipitated with an efficiency of 73%. The overall vanadium extraction efficiency was 70% [38].

Due to the high consumption of chemicals in leaching operations and the need for a high amount of energy, which causes  $SO_2$  gas emissions in pyrometallurgical processes, the bio-hydrometallurgical methods are developed based on the microorganisms (bacteria or fungi) leaching [42]. The advantages of bioleaching include Environmentally friendly, low cost, easy leaching at room temperature and atmospheric pressure, applicable to low-grade ores or wastes, and adaptation to high concentrations of toxic heavy metals [42].

Bioleaching of the spent petroleum catalyst with Fe/S oxidizing bacteria (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*) extracted 90% of the vanadium in

two-step leaching [42]. Pradhan et al. investigated metals dissolution from the spent catalyst. In this study, about 95% of vanadium is leached out from a spent catalyst by adapted *Acidithiobacillus ferrooxidans* [113]. In another study, Mikoda et al. applied citric acid leaching and bioleaching with *Acidithiobacillus thiooxidans* on the spent sulfuric acid catalyst for vanadium extraction. This method can be leached out nearly 96% of vanadium [114]. In addition, bioleaching methods have been tested for vanadium extraction from the stone coal by bacillus mucilaginosus [115], vanadium-bearing titanomagnetite [116], steel slag by *Acidithiobacillus ferrooxidans*, and *Acidithiobacillus thiooxidans* [116-117] and red mud by fungi *A. niger* and *Penicillium tricolor* [118].

However, despite the benefits of biotechnology, this method is still sensitive to industrial and commercial applications, and much more research is needed for this purpose and more sustainable recovery of vanadium [119].

#### 6.4. Vanadium extraction from vanadium-containing wastewater

Using ammonium salts for the precipitation of vanadium during traditional methods, a large amount of vanadium wastewater is produced which contains vanadium, high amounts of ammonium, and impurity ions. Zhu et al. used strongly basic anionic resin 717 (201\*7) for the removal of vanadium from vanadium wastewater. In this study, the 201\*7 resin has been able to adsorb up to 99% of vanadium under the conditions of a pH value of 6-8, a temperature of 40°C, and a time of 20 min [105,106].

Ying et al. applied acid leaching (acid sulfuric as the reagent) under the atmosphere and pressurized the calcium roasting-acid leaching tailing. In this study, approximately 92% of vanadium was extracted using pressurized leaching under optimum conditions, while in the atmospheric leaching only 29-43% of vanadium was extracted. The results of X-ray photoelectron spectroscopy (XPS) analysis indicate that vanadium is present in the tailings in the form of V(IV), V(V), and the rest of it existed in the form of V(III). However, breaking the vanadium phases is difficult for atmospheric leaching. The advantages of this environmentally friendly method include the removal of toxic vanadium ions (V(III), V(V)) from the tailings, breaking vanadium spinel, calcium sulfate dehydrate, carmichaelite (A combination of Al, V, Fe, Ti, Cr, Mg, O elements) and easy vanadium leaching under pressure. [104].

Muthukumar et al. developed a simple and economical process (Figure 24) to extract vanadium from the calcium vanadate sludge produced during spent catalyst processing, using ammonium sulfate. 82% of vanadium is leached out by ammonium sulfate under optimum

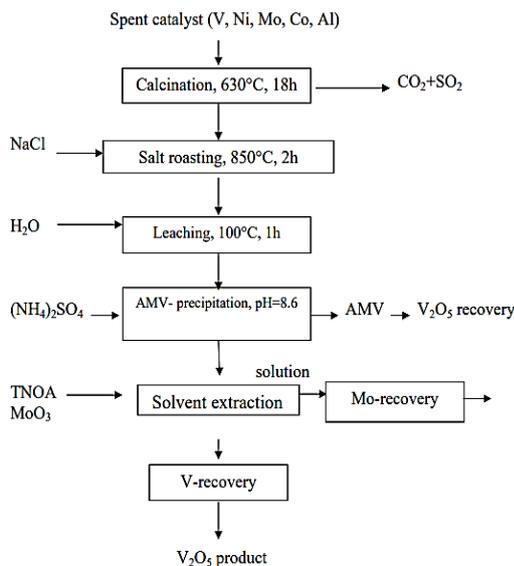


Figure 23. Salt roasting and water leaching process for recovery of vanadium from spent catalyst [5].

conditions. In comparison with the sulfuric acid leaching method, ammonium sulfate leaching has some advantages such as selectively vanadium recovery, low cost, no step for impurity removal, and AMV product with desirable quality (98.5%) [110].

## 7. Conclusion

In this article, industrial and proposed novel methods have been reviewed for the extraction of vanadium pentoxide from primary, secondary, and co-product sources. Due to the lack of vanadium ores in nature, the sources of vanadium are diverse and often extracted from vanadium-bearing titanomagnetite reserves. In addition, in China, stone coal is another reliable primary source of vanadium due to the high demand for vanadium and the significant amount of reserves. The mineral processing operations are widely used to beneficiation of titanomagnetite ores. However, the proposed methods to produce vanadium concentrate from stone coal have low vanadium recovery due to the complex stone coal structure and low grade of vanadium that require the attention of researchers.

The traditional sodium roasting-water leaching process is still a selective, industrial, economical, and mature method for the production of fine-grade vanadium pentoxide due to its easy, stable operation and high recovery of vanadium. However, this process suffers from environmental pollution such as releasing corrosive gases, and the generation of large volumes of high-alkali wastewater which threatens the development of the vanadium industry. Therefore, new technologies have been proposed for the efficient and clean production of vanadium pentoxide. All alternative processes have disadvantages and industrial development of these methods will not be easy due to the complexity of extraction characteristics. Therefore, more investment and research are needed for the industrial development of these processes.

Alkaline or acid leaching is not used in titanomagnetite treatment. Acid leaching has high efficiency and has been mainly used in uranium-vanadium ores, fly ashes, and boiler ashes by the sulfuric acid reagent. But alkaline leaching has a high selection over acid leaching but has been less used in vanadium processing and mainly treated high lime uranium-vanadium ore with sodium carbonate, fly ash, boiler ash, and spent catalysts with sodium hydroxide.

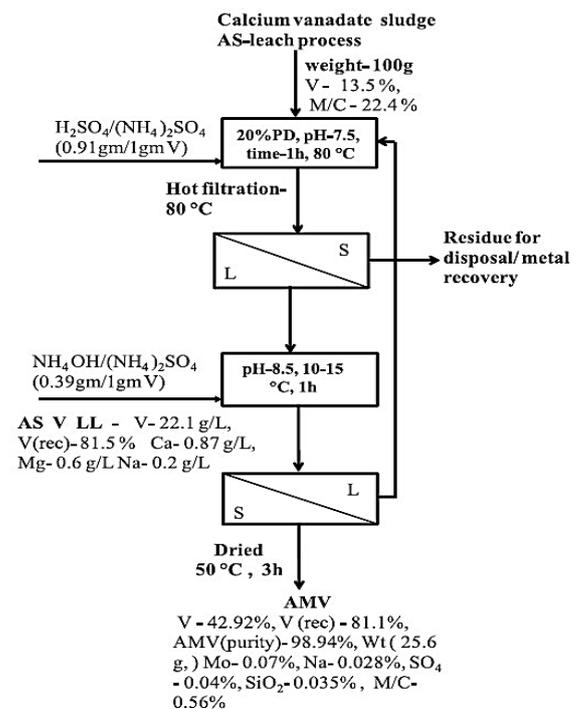


Figure 24. Flowsheet of the ammonium sulfate leaching process for AMV production [110].

Vanadium leach liquors are usually impure and a purification step is necessary. Presently, the simple and lower-cost chemical precipitation is applied to leach liquor (containing relatively simple impurities) that is obtained by the sodium roasting-water leaching process at vanadium processing plants. However, solvent extraction or ion exchange method are commercially used for complex or dilute solutions obtained from the stone coal and spent catalyst. In addition, still, there are problems in the purification of the leach liquors that are obtained by proposed and new vanadium extraction methods.

The significant amount of acclimated hazardous vanadium-containing industrial (fly ash, spent catalyst, etc.) wastes have good potential for extraction of vanadium pentoxide. Numerous hydrometallurgical and pyrometallurgical processes have been developed on the industrial and laboratory scale for vanadium extraction and other valuable elements.

In addition, bio-hydrometallurgical methods are proposed for the environment-friendly extraction of vanadium. However, considering the advantages of hydrometallurgical and bio-hydrometallurgical processes, the development of a new commercial procedure for the highly efficient utilization of raw materials and clean production is necessary.

In the future, vanadium will play a critical role in developing high-performance and clean VRB batteries. As the vanadium market grows, the development of new factories to produce vanadium will increase. Therefore, vanadium extraction technology will be directed towards high-efficiency processes with a lower environmental footprint.

## REFERENCES

- [1] Del Carpio, E., Hernández, L., Ciangherotti, C., Coa, V. V., Jiménez, L., Lubes, V., & Lubes, G. (2018). Vanadium: History, chemistry, interactions with  $\alpha$ -amino acids and potential therapeutic applications. *Coordination chemistry reviews*, 372, 117-140.
- [2] Moskalyk, R. R., & Alfantazi, A. M. (2003). Processing of vanadium: a review. *Minerals engineering*, 16(9), 793-805.
- [3] Imtiaz, M., Rizwan, M. S., Xiong, S., Li, H., Ashraf, M., Shahzad, S. M., & Tu, S. (2015). Vanadium, recent advancements, and research prospects: a review. *Environment International*, 80, 79-88.
- [4] Gilligan, R., & Nikoloski, A. N. (2020). The extraction of vanadium from titanomagnetites and other sources. *Minerals Engineering*, 146, 106106.
- [5] Ye, G. (2006). Recovery of Vanadium from LD slag. A state of the art report, Part 1 - Facts and metallurgy of Vanadium. *Development*, 816.
- [6] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Vanadium and its compounds. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 9-32). Elsevier.
- [7] Habashi, F. (1977). *Handbook of Extractive Metallurgy—Volume: III*.
- [8] Pessoa, J. C., Etcheverry, S., & Gambino, D. (2015). Vanadium compounds in medicine. *Coordination Chemistry Reviews*, 301, 24-48.
- [9] Okudan, M. D., Akcil, A., Tuncuk, A., & Devenci, H. (2015). Effect of parameters on vanadium recovery from by-products of the Bayer process. *Hydrometallurgy*, 152, 76-83.
- [10] Gaudet, P. (2017, October 3). *U3O8 Corp. Highlights Planned Production Profile for Vanadium from the Laguna Salada Deposit Based on a PEA*. U3O8 Corp. Retrieved July 15, 2021, from <http://www.u3o8corp.com/u3o8-corp-highlights-planned-production-profile-for-vanadium-from-the-laguna-salada-deposit-based-on-a-pea/>
- [11] Ferro-Alloy Resources Group. (2020, July 30). *vanadium market overview*. Retrieved October 20, 2020, from <http://www.ferro-alloy.com/en/vanadium/vanadium-market-overview/>
- [12] Zhang, Y. M., Bao, S. X., Liu, T., Chen, T. J., & Huang, J. (2011). The technology of extracting vanadium from stone coal in China: History, current status and future prospects. *Hydrometallurgy*, 109(1-2), 116-124.
- [13] *About Vanadium – Bushveld Minerals*. (n.d.). Retrieved July 22, 2021, from <https://www.bushveldminerals.com/about-vanadium/>
- [14] Li, X., Wei, C., Deng, Z., Li, M., Li, C., & Fan, G. (2011). Selective solvent extraction of vanadium over iron from a stone coal/black shale acid leach solution by D2EHPA/TBP. *Hydrometallurgy*, 105(3-4), 359-363.
- [15] Gao, F., Olayiwola, A. U., Liu, B., Wang, S., Du, H., Li, J., ... & Zhang, Y. (2021). Review of Vanadium Production Part I: Primary Resources. *Mineral Processing and Extractive Metallurgy Review*, 1-23.
- [16] Li, H. Y., Wang, C. J., Yuan, Y. H., Guo, Y., Diao, J., & Xie, B. (2020). Magnesiation roasting-acid leaching: A zero-discharge method for vanadium extraction from vanadium slag. *Journal of Cleaner Production*, 260, 121091.
- [17] Xiao, Y., Jalkanen, H., Yang, Y., Mambote, C. R., & Boom, R. (2010). Ferrovandium production from petroleum fly ash and BOF flue dust. *Minerals Engineering*, 23(14), 1155-1157.
- [18] Gupta, C. K., & Krishnamurthy, N. (1992). Sources processing. In *Extractive Metallurgy of vanadium* (pp. 203-381). Elsevier.
- [19] Le, M. N., & Lee, M. S. (2021). A review on hydrometallurgical processes for the recovery of valuable metals from spent catalysts and life cycle analysis perspective. *Mineral Processing and Extractive Metallurgy Review*, 42(5), 335-354.
- [20] Zhu, X., Li, W., Tang, S., Zeng, M., Bai, P., & Chen, L. (2017). Selective recovery of vanadium and scandium by ion exchange with D201 and solvent extraction using P507 from hydrochloric acid leaching solution of red mud. *Chemosphere*, 175, 365-372.
- [21] Crabtree, E. H., & Smith, F. L. (1961). Mining and western world sources of vanadium. *Journal of the Less Common Metals*, 3(6), 433-436.
- [22] Zhang, G., Luo, D., Deng, C., Lv, L., Liang, B., & Li, C. (2018). Simultaneous extraction of vanadium and titanium from vanadium slag using ammonium sulfate roasting-leaching process. *Journal of Alloys and Compounds*, 742, 504-511.
- [23] Mahdilu, A., Gaffari, S., Irannejad, M. (2008). Extraction of Vanadium from Ghara Aghaj titanomagnetite by roasting-leaching Method. *Scientific-Research Journal of Mining Engineering* 3(6), 9-17.
- [24] Taylor, P. R., Shuey, S. A., Vidal, E. E., & Gomez, J. C. (2006). Extractive metallurgy of vanadium-containing titaniferous magnetite ores: a review. *Mining, Metallurgy & Exploration*, 23(2), 80-86.
- [25] Zhou, X., Li, C., Li, J., Liu, H., & Wu, S. (2009). Leaching of vanadium from carbonaceous shale. *Hydrometallurgy*, 99(1-2), 97-99.
- [26] Peng, H. (2019). A literature review on leaching and recovery of vanadium. *Journal of Environmental Chemical Engineering*, 7(5), 103313.
- [27] Zhang, G., Zhang, Y., Bao, S., Jian, X., & Li, R. (2019). Selective vanadium extraction from vanadium bearing ferro-phosphorus via roasting and pressure hydrogen reduction. *Separation and*

*Purification Technology*, 220, 293-299.

- [28] Rollmann, L. D., & Walsh, D. E. (1980). *U.S. Patent No. 4,203,830*. Washington, DC: U.S. Patent and Trademark Office.
- [29] Eidem, P. K. (1988). *Reducing the metals content of petroleum feedstocks* (No. US 4752382).
- [30] Salehzadeh, H., Mousavi, M., HATAMI, P. S., & Kermanshahi, K. (2007). Microbial demetallization of crude oil using *Aspergillus* sp.: vanadium oxide octaethyl porphyrin (VOOEP) as a model of metallic petroporphyrins.
- [31] Barin, R., Salehzadeh, H. (2012). Demetallization of crude oil with emphasis on biotechnology strategies. *Iranian Journal of Chemical Engineering*, 22-31.
- [32] Vitolo, S., Seggiani, M., Filippi, S., & Brocchini, C. (2000). Recovery of vanadium from heavy oil and Orimulsion fly ashes. *Hydrometallurgy*, 57(2), 141-149.
- [33] Liu, Z., & Li, H. (2015). Metallurgical process for valuable elements recovery from red mud—A review. *Hydrometallurgy*, 155, 29-43.
- [34] Mukherjee, T. K., Chakraborty, S. P., Bidaye, A. C., & Gupta, C. K. (1990). Recovery of pure vanadium oxide from bayer sludge. *Minerals Engineering*, 3(3-4), 345-353.
- [35] Liu, Y., & Naidu, R. (2014). Hidden values in bauxite residue (red mud): Recovery of metals. *Waste management*, 34(12), 2662-2673.
- [36] Erust, C., Akcil, A., Bedelova, Z., Anarbekov, K., Baikonurova, A., & Tuncuk, A. (2016). Recovery of vanadium from spent catalysts of sulfuric acid plant by using inorganic and organic acids: laboratory and semi-pilot tests. *Waste Management*, 49, 455-461.
- [37] Kim, H. I., Lee, K. W., Mishra, D., Yi, K. M., Hong, J. H., Jun, M. K., & Park, H. K. (2014). Separation and recovery of vanadium from leached solution of spent residuehydrodesulfurization (RHDS) catalyst using solvent extraction. *Journal of Industrial and Engineering Chemistry*, 20(6), 4457-4462.
- [38] Khorfan, S., Wahoud, A., & Reda, Y. (2001). Recovery of vanadium pentoxide from spent catalyst used in the manufacture of sulphuric acid. *Periodica Polytechnica Chemical Engineering*, 45(2), 131-137.
- [39] Mulak, W., Szymczycha, A., Lesniewicz, A., & Zyrnicki, W. (2006). Preliminary results of metals leaching from a spent hydrodesulfurization (HDS) catalyst. *Physicochemical Problems of Mineral Processing*, 40, 69-76.
- [40] Beolchini, F., Fonti, V., Ferella, F., & Vegliò, F. (2010). Metal recovery from spent refinery catalysts by means of biotechnological strategies. *Journal of Hazardous Materials*, 178(1-3), 529-534.
- [41] Mishra, D., Kim, D. J., Ralph, D. E., Ahn, J. G., & Rhee, Y. H. (2007). Bioleaching of vanadium rich spent refinery catalysts using sulfur oxidizing lithotrophs. *Hydrometallurgy*, 1(88), 202-209.
- [42] Akcil, A., Vegliò, F., Ferella, F., Okudan, M. D., & Tuncuk, A. (2015). A review of metal recovery from spent petroleum catalysts and ash. *Waste Management*, 45, 420-433.
- [43] Emami, A.H. (2002). Extraction of vanadium from slag of Isfahan Zobahan steel converter, *MSc thesis*.
- [44] Aarabi-Karasgani, M., Rashchi, F., Mostoufi, N., & Vahidi, E. (2010). Leaching of vanadium from LD converter slag using sulfuric acid. *Hydrometallurgy*, 102(1-4), 14-21.
- [45] Mirazimi, S. M. J., Rashchi, F., & Saba, M. (2013). Vanadium removal from roasted LD converter slag: Optimization of parameters by response surface methodology (RSM). *Separation and Purification Technology*, 116, 175-183.
- [46] Hedayati, S. (2017). Purification of vanadium leaching solution from steel converter slag by solvent extraction method. *MSc thesis*.
- [47] Abbasi, M. H., & Safarnoorallah, M. (1998). Extraction of Vanadium Oxide from Boiler Fuel Ash. *Computational Methods in Engineering*, 17(1), 165-175.
- [48] Nazari, E. (2014). Recovery of vanadium and nickle from the fuel ash of power plants. *MSc thesis*.
- [49] Bafegi, M., AbuTalebi, M. R., Emami, A. H. (2005). recovery of vanadium from steel converter overhead by salt leaching method. *Journal of the Faculty of Engineering*, 813-820.
- [50] Amadeh, A. A., Paydar, M. H., Attayi, A., Emami, M., Vegar, R. (2000). Improvement of Kahnooj Titanium Mine Concentrate by Slag Method, *Journal of the Faculty of Engineering*, 43-35.
- [51] Tabatabayi, A., Karimi, G. (2004). Recovery and Extraction of Vanadium from Choghart Iron Ore, *Iran Mining Engineering Conference*, 19-1.
- [52] Fallah, Z., Tagizadeh, M., Godosinejad, D. (2016). Extraction of vanadium from Saghand ores in Yazd by salt roasting- acid leaching method. *Iranian Journal of Chemistry and Chemical Engineering*, 73-81.
- [53] Hosseinzadeh, M., Alizadeh, M., & Raouf Hosseini, S. M. (2017). Mineralogical and physical beneficiation studies for iron extraction from Bardaskan titanomagnetite placer deposit. *Journal of Mining and Environment*, 8(2), 191-201.
- [54] Alizadeh, M. (2015). Design of titanium magnetite placer sand processing process for simultaneous extraction of vanadium, titanium and iron elements. *Quarterly Journal of Advanced Materials and Technologies*, 36-27.
- [55] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Extraction of vanadium from titaniferous magnetite: mineral processing and enrichment methods. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 59–88). Elsevier.
- [56] Wang, M., Huang, S., Chen, B., & Wang, X. (2020). A review of processing technologies for vanadium extraction from stone coal. *Mineral Processing and Extractive Metallurgy*, 129(3-4), 290-298.
- [57] Nkosi, S., Dire, P., Nyambeni, N., & Goso, X. C. (2017). A comparative study of vanadium recovery from titaniferous magnetite using salt, sulphate, and soda ash roast-leach processes. In *3rd Young Professionals Conference* (pp. 191-200).
- [58] Wang, Z. H., Zheng, S. L., Wang, S. N., Biao, L. I. U., Wang, D. W., Hao, D. U., & 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.
- [59] Chen, D., Zhao, L., Liu, Y., Qi, T., Wang, J., & Wang, L. (2013). A novel process for recovery of iron, titanium, and vanadium from titanomagnetite concentrates: NaOH molten salt roasting and water leaching processes. *Journal of hazardous materials*, 244, 588-595.
- [60] Ji, Y., Shen, S., Liu, J., & Xue, Y. (2017). Cleaner and effective process for extracting vanadium from vanadium slag by using an innovative three-phase roasting reaction. *Journal of cleaner production*, 149, 1068-1078.

- [61] Li, M., Liu, B., Zheng, S., Wang, S., Du, H., Dreisinger, D. B., & Zhang, Y. (2017). A cleaner vanadium extraction method featuring non-salt roasting and ammonium bicarbonate leaching. *Journal of cleaner production*, 149, 206-217.
- [62] Xiang, J., Huang, Q., Lv, X., & Bai, C. (2018). Extraction of vanadium from converter slag by two-step sulfuric acid leaching process. *Journal of Cleaner Production*, 170, 1089-1101.
- [63] Li, R., Liu, T., Zhang, Y., Huang, J., & Xu, C. (2018). Efficient extraction of vanadium from vanadium-Titanium magnetite concentrate by potassium salt roasting additives. *Minerals*, 8(1), 25.
- [64] Wen, J., Jiang, T., Wang, J., Lu, L., & Sun, H. (2020). Cleaner extraction of vanadium from vanadium-chromium slag based on MnO<sub>2</sub> roasting and manganese recycle. *Journal of Cleaner Production*, 261, 121205.
- [65] Navarro, R., Guzman, J., Saucedo, I., Revilla, J., & Guibal, E. (2007). Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. *Waste Management*, 27(3), 425-438.
- [66] Ju, Z. J., Wang, C. Y., & Yin, F. (2015). Dissolution kinetics of vanadium from black shale by activated sulfuric acid leaching in atmosphere pressure. *International Journal of Mineral Processing*, 138, 1-5.
- [67] Jiang, D., Song, N., Liao, S., Lian, Y., Ma, J., & Jia, Q. (2015). Study on the synergistic extraction of vanadium by mixtures of acidic organophosphorus extractants and primary amine N1923. *Separation and Purification Technology*, 156, 835-840.
- [68] Yang, X., Zhang, Y., Bao, S., & Shen, C. (2016). Separation and recovery of vanadium from a sulfuric-acid leaching solution of stone coal by solvent extraction using trialkylamine. *Separation and Purification Technology*, 164, 49-55.
- [69] Zhu, Z., Tulpatowicz, K., Pranolo, Y., & Cheng, C. Y. (2015). Solvent extraction of molybdenum and vanadium from sulphate solutions with Cyphos IL 101. *Hydrometallurgy*, 154, 72-77.
- [70] Zhang, P., Inoue, K., Yoshizuka, K., & Tsuyama, H. (1996). Extraction and selective stripping of molybdenum (VI) and vanadium (IV) from sulfuric acid solution containing aluminum (III), cobalt (II), nickel (II) and iron (III) by LIX 63 in Exxsol D80. *Hydrometallurgy*, 41(1), 45-53.
- [71] Zhu, X. Z., Huo, G. S., Jie, N. I., & Qiong, S. O. N. G. (2017). Removal of tungsten and vanadium from molybdate solutions using ion exchange resin. *Transactions of Nonferrous Metals Society of China*, 27(12), 2727-2732.
- [72] Wang, X., Wang, M., Shi, L., Hu, J., & Qiao, P. (2010). Recovery of vanadium during ammonium molybdate production using ion exchange. *Hydrometallurgy*, 104(2), 317-321.
- [73] Chen, D., Zhao, H., Hu, G., Qi, T., Yu, H., Zhang, G., ... & Wang, W. (2015). An extraction process to recover vanadium from low-grade vanadium-bearing titanomagnetite. *Journal of hazardous materials*, 294, 35-40.
- [74] Zeng, L., & Cheng, C. Y. (2010). Recovery of molybdenum and vanadium from synthetic sulphuric acid leach solutions of spent hydrodesulphurisation catalysts using solvent extraction. *Hydrometallurgy*, 101(3-4), 141-147.
- [75] Xie, F., Zhang, T. A., Dreisinger, D., & Doyle, F. (2014). A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering*, 56, 10-28.
- [76] Hao, X. C. (2018). Extraction of vanadium from acidic leaching of waste vanadium-catalyst using ion-exchange resin. *Hydrometallurgy of China*, 37, 281-285.
- [77] Bao, S., Duan, J., & Zhang, Y. (2018). Recovery of V (V) from complex vanadium solution using capacitive deionization (CDI) with resin/carbon composite electrode. *Chemosphere*, 208, 14-20.
- [78] Zeng, L., Li, Q., & Xiao, L. (2009). Extraction of vanadium from the leach solution of stone coal using ion exchange resin. *Hydrometallurgy*, 97(3-4), 194-197.
- [79] Pan, B., Liu, B., Wang, S., Wenzel, M., Weigand, J. J., Feng, M., ... & Zhang, Y. (2020). Ammonium vanadate/ammonia precipitation for vanadium production from a high vanadate to sodium ratio solution obtained via membrane electrolysis method. *Journal of Cleaner Production*, 263, 121357.
- [80] Zhang, J. H., Zhang, W., Zhang, L., & Gu, S. Q. (2014). A critical review of technology for selective recovery of vanadium from leaching solution in V<sub>2</sub>O<sub>5</sub> production. *Solvent extraction and ion exchange*, 32(3), 221-248.
- [81] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Extraction of vanadium from V-containing titaniferous magnetite: extraction of V<sub>2</sub>O<sub>5</sub> from vanadium slag. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 149-199). Elsevier.
- [82] Pan, B., Jin, W., Liu, B., Zheng, S., Wang, S., Du, H., & Zhang, Y. (2017). Cleaner production of vanadium oxides by cation-exchange membrane-assisted electrolysis of sodium vanadate solution. *Hydrometallurgy*, 169, 440-446.
- [83] Pan, B., Du, H., Wang, S., Wang, H., Liu, B., & Zhang, Y. (2019). Cleaner production of ammonium poly-vanadate by membrane electrolysis of sodium vanadate solution: The effect of membrane materials and electrode arrangements. *Journal of Cleaner Production*, 239, 118129.
- [84] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Extracting vanadium pentoxide from minerals and composite materials containing vanadium. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 227-242). Elsevier.
- [85] Janzadeh, A., Ketabchi, A., Sadrnejad, S. A., Baddei, R. (1384). Extraction of vanadium from spent catalysts and vanadium containing ore, as available vanadium containing raw materials in Iran. *Chemistry and Chemical Engineering of Iran*.
- [86] Crabtree, E. H., & Padilla, V. E. (1961). The treatment of vanadium ores for the recovery of vanadium pentoxide. *Journal of the Less Common Metals*, 3(6), 437-442.
- [87] Zhang, Y. M., Wang, L. N., Chen, D. S., Wang, W. J., Liu, Y. H., Zhao, H. X., & Qi, T. (2018). A method for recovery of iron, titanium, and vanadium from vanadium-bearing titanomagnetite. *International Journal of Minerals, Metallurgy, and Materials*, 25(2), 131-144.
- [88] Bian, Z., Feng, Y., Li, H., & Wu, H. (2021). Efficient separation of vanadium, titanium, and iron from vanadium-bearing titanomagnetite by pressurized pyrolysis of ammonium chloride-acid leaching-solvent extraction process. *Separation and Purification Technology*, 255, 117169.
- [89] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Extraction of vanadium from V-bearing titaniferous magnetite by smelting to produce V-containing iron. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 89-121). Elsevier.
- [90] Mahdavian, A., Shafyei, A., Keshavarz Alamdari, E., & Haghshenas, D. F. (2006). Recovery of vanadium from Esfahan Steel Company steel slag: optimizing of roasting and leaching parameters. *International Journal of Iron & Steel Society of Iran*, 3(2), 17-21.

- [91] Nasimifar, A. R., & Mehrabani, J. V. (2021). Comparison of different processes for the production of vanadium pentoxide from vanadium-containing sources. *First International Conference on Metallurgical, Mechanical and Mining Engineering*.
- [92] Zhang, J., Zhang, W., & Xue, Z. (2019). An environment-friendly process featuring calcified roasting and precipitation purification to prepare vanadium pentoxide from the converter vanadium slag. *Metals*, 9(1), 21.
- [93] Du, G., Fan, C., Yang, H., & Zhu, Q. (2019). Selective extraction of vanadium from pre-oxidized vanadium slag by carbochlorination in fluidized bed reactor. *Journal of Cleaner Production*, 237, 117765.
- [94] Jiang, D. D., Zhang, H. L., Xu, H. B., & Zhang, Y. (2017). Chlorination and purification of vanadium pentoxide with anhydrous aluminum chloride. *Journal of Alloys and Compounds*, 709, 505-510.
- [95] Mink, G., Bertóti, I., Battistoni, C., & Székely, T. (1985). Chlorination of V<sub>2</sub>O<sub>5</sub> by CCl<sub>4</sub>. The proposed reaction mechanism. *Reaction Kinetics and Catalysis Letters*, 27(1), 39-45.
- [96] Zheng, H. Y., Sun, Y., Lu, J. W., Dong, J. H., Zhang, W. L., & Shen, F. M. (2017). Vanadium extraction from vanadium-bearing titanomagnetite by selective chlorination using chloride wastes (FeCl<sub>x</sub>). *Journal of Central South University*, 24(2), 311-317.
- [97] Wang, T., Xu, L., Liu, C., & Zhang, Z. (2014). Calcified roasting-acid leaching process of vanadium from low-grade vanadium-containing stone coal. *Chinese Journal of Geochemistry*, 33(2), 163-167.
- [98] Liu, Y. H., Yang, C., Li, P. Y., & Li, S. Q. (2010). A new process of extracting vanadium from stone coal. *International Journal of Minerals, Metallurgy, and Materials*, 17(4), 381-388.
- [99] Deng, Z. G., Chang, W. E. I., Gang, F. A. N., Li, M. T., Li, C. X., & Li, X. B. (2010). Extracting vanadium from stone-coal by oxygen pressure acid leaching and solvent extraction. *Transactions of Nonferrous Metals Society of China*, 20, s118-s122.
- [100] Zeng, L., & Cheng, C. Y. (2009). A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts: Part II: Separation and purification. *Hydrometallurgy*, 98(1-2), 10-20.
- [101] El-Nadi, Y. A., Awwad, N. S., & Nayl, A. A. (2009). A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst. *International Journal of Mineral Processing*, 92(3-4), 115-120.
- [102] Li, W., Zhang, Y., Liu, T., Huang, J., & Wang, Y. (2013). Comparison of ion exchange and solvent extraction in recovering vanadium from sulfuric acid leach solutions of stone coal. *Hydrometallurgy*, 131, 1-7.
- [103] Li, M., Wei, C., Fan, G., Li, C., Deng, Z., & Li, X. (2009). Extraction of vanadium from shale using pressure acid leaching. *Hydrometallurgy*, 98(3-4), 308-313.
- [104] Yang, B., He, J., Zhang, G., & Guo, J. (2021). Extracting vanadium from shale. In *Vanadium: Extraction, Manufacturing and Applications* (pp. 201–225). Elsevier.
- [105] Zhang, Y., Zhang, T. A., Dreisinger, D., Lv, C., Lv, G., & Zhang, W. (2019). Recovery of vanadium from calcification roasted-acid leaching tailing by enhanced acid leaching. *Journal of hazardous materials*, 369, 632-641.
- [106] Zhu, X., Li, W., & Zhang, C. (2020). Extraction and removal of vanadium by adsorption with resin 201\* 7 from vanadium waste liquid. *Environmental research*, 180, 108865.
- [107] Makhotkina, E. S., & Shubina, M. V. (2017). Industrial, Ecological and Resource-Efficient Aspects of Vanadium Production and Use of Technogenic Vanadium Sources. In *Solid State Phenomena* (Vol. 265, pp. 994-998). Trans Tech Publications Ltd.
- [108] Tsai, S. L., & Tsai, M. S. (1998). A study of the extraction of vanadium and nickel in oil-fired fly ash. *Resources, conservation and recycling*, 22(3-4), 163-176.
- [109] Abdel-latif, M. A. (2002). Recovery of vanadium and nickel from petroleum flyash. *Minerals Engineering*, 15(11), 953-961.
- [110] Muthukumar, K., Patel, K. M., Mohapatra, D., Padh, B., & Reddy, B. R. (2020). Selective recovery of vanadium as AMV from calcium vanadate sludge by direct AS leaching process: An industrial approach. *Waste Management*, 102, 815-822.
- [111] Nazari, E., Rashchi, F., Saba, M., & Mirazimi, S. M. J. (2014). Simultaneous recovery of vanadium and nickel from power plant fly-ash: Optimization of parameters using response surface methodology. *Waste management*, 34(12), 2687-2696.
- [112] Mohanty, J., Rath, P. C., Bhattacharya, I. N., & Paramguru, R. K. (2011). The recovery of vanadium from spent catalyst: a case study. *Mineral Processing and Extractive Metallurgy*, 120(1), 56-60.
- [113] Pradhan, D., Sukla, L. B., Pattanaik, A., Samal, D. K., Biswal, T., & Jena, S. K. B. (2021). Improvement in metal dissolution from spent catalyst by adapted *Acidithiobacillus ferrooxidans*. *Biointerface Res. Appl. Chem*, 11, 7794-7803.
- [114] Mikoda, B., Potysz, A., Gruszecka-Kosowska, A., Kmiecik, E., & Tomczyk, A. (2020). Spent sulfuric acid plant catalyst: valuable resource of vanadium or risky residue? Process comparison for environmental implications. *Environmental Science and Pollution Research*, 1-10.
- [115] Dong, Y., Lin, H., Liu, Y., & Zhao, Y. (2020). Blank roasting and bioleaching of stone coal for vanadium recycling. *Journal of Cleaner Production*, 243, 118625.
- [116] Li, J., Zhang, B., Yang, M., & Lin, H. (2021). Bioleaching of vanadium by *Acidithiobacillus ferrooxidans* from vanadium-bearing resources: Performance and mechanisms. *Journal of Hazardous Materials*, 416, 125843.
- [117] Gomes, H. I., Funari, V., Mayes, W. M., Rogerson, M., & Prior, T. J. (2018). Recovery of Al, Cr and V from steel slag by bioleaching: batch and column experiments. *Journal of environmental management*, 222, 30-36.
- [118] Qu, Y., Li, H., Wang, X., Tian, W., Shi, B., Yao, M., ... & Yue, L. (2019). Selective parameters and bioleaching kinetics for leaching vanadium from red mud using *Aspergillus niger* and *Penicillium tricolor*. *Minerals*, 9(11), 697.
- [119] Zeng, L., & Cheng, C. Y. (2009). A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts: Part I: Metallurgical processes. *Hydrometallurgy*, 98(1-2), 1-9.
- [120] Rojas-Rodríguez, A. D., Flores-Fajardo, O., González, F. S. A., Castillo, N. N. L., & Gómez, M. J. C. (2012). Chemical treatment to recover molybdenum and vanadium from spent heavy gasoil hydrodesulfurization catalyst.
- [121] Chen, Y., Feng, Q., Shao, Y., Zhang, G., Ou, L., & Lu, Y. (2006). Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst. *International Journal of Mineral Processing*, 79(1), 42-48.

- [122] Ognyanova, A., Ozturk, A. T., De Michelis, I., Ferella, F., Taglieri, G., Akcil, A., & Vegliò, F. (2009). Metal extraction from spent sulfuric acid catalyst through alkaline and acidic leaching. *Hydrometallurgy*, 100(1-2), 20-28.
- [123] Huo, Y., Chang, Z., Li, W., Liu, S., & Dong, B. (2015). Reuse and valorization of vanadium and tungsten from waste V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst. *Waste and Biomass Valorization*, 6(2), 159-165.
- [124] Mazurek, K. (2013). Recovery of vanadium, potassium and iron from a spent vanadium catalyst by oxalic acid solution leaching, precipitation and ion exchange processes. *Hydrometallurgy*, 134, 26-31.