Review

Extraction of the Rare Element Vanadium from Vanadium-Containing Materials by Chlorination Method: A Critical Review

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Abstract: Vanadium as a rare element has a wide range of applications in iron and steel production, vanadium flow batteries, catalysts, etc. In 2018, the world's total vanadium output calculated in the form of metal vanadium was 91,844 t. The raw materials for the production of vanadium products mainly include vanadium-titanium magnetite, vanadium slag, stone coal, petroleum coke, fly ash, and spent catalysts, etc. Chlorinated metallurgy has a wide range of applications in the treatment of ore, slag, solid wastes, etc. Chlorinating agent plays an important role in chlorination metallurgy, which is divided into solid (NaCl , KCl , CaCl_2 , AlCl_3 , FeCl_2 , FeCl_3 , MgCl_2 , NH_4Cl , NaClO , and NaClO_3) and gas (Cl_2 , HCl , and CCl_4). The chlorination of vanadium oxides (V_2O_3 and V_2O_5) by different chlorinating agents was investigated from the thermodynamics. Meanwhile, this paper summarizes the research progress of chlorination in the treatment of vanadium-containing materials. This paper has important reference significance for further adopting the chlorination method to treat vanadium-containing raw materials.

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1. Introduction

Vanadium is located in the fourth period and fifth (VB) group of the periodic table and which occupies the 23rd position in the periodic table of elements. The symbol of the vanadium element is V. The physical characteristics of vanadium are a melting point of 1929°C , boiling point of 3350°C , relative atomic mass of 50.9415, and density of 5.96 g/cm^3 , and it is a silver grey metal [1,2]. The valence of vanadium in compounds can be +2, +3, +4, and +5 [3]. At present, there are known vanadium oxides such as V_2O_3 , VO_2 , V_2O_5 , V_3O_5 , V_3O_7 , V_4O_7 , V_5O_9 , V_6O_{11} , and V_6O_{13} , among which the pentavalent vanadium compounds are the most stable [4]. The main chlorides are VOCl_3 , VOCl , VCl_5 , VCl_4 , VCl_3 , VCl_2 , and VCl , among which VOCl_3 are the most stable [5]. However, the toxicity of vanadium compounds increases with the increase of vanadium valence, and the pentavalent vanadium compounds are the most toxic. Thus, compounds containing pentavalent vanadium, such as NaVO_3 , NH_4VO_3 , V_2O_5 , and VOCl_3 , are the most toxic [6]. Toxic vanadium compounds can exist in both cationic and anionic forms [7].

Vanadium as a rare element has a wide range of applications in iron and steel production, vanadium flow batteries, catalysts, etc. [8,9]. The raw materials for the production of vanadium products mainly include vanadium-titanium magnetite, vanadium slag, stone coal, petroleum coke, fly ash, and spent catalysts, etc. [1,8,9]. Salt roasting (Na_2CO_3 , NaCl , NaOH , CaO , etc.) was applied to extract vanadium from vanadium-containing materials [1,8,9]. However, the salt roasting method extraction of vanadium from vanadium slag is associated with the formation of a large amount of sludge and significant losses of vanadium [10]. Previous review articles on vanadium extraction from vanadium-containing

materials mainly focused on the salt roasting process [1,8,9]. In this work, extraction of the rare element vanadium from vanadium-containing materials by chlorination method was summarized.

Table 1 shows melting temperature, boiling temperature, and sublimation temperature for vanadium compounds [11,12]. According to Table 1, the melting point and boiling point of chloride are lower than those of corresponding oxides. Thus, chloride is easier to separate and enrich than oxide [13–15]. Chlorinated metallurgy has a wide range of applications in the treatment of ore, slag, solid wastes, etc. [16–22]. In the last century, the extraction of Ti from titanium ore by chlorination method has been industrialized [23]. Chlorinating agent plays an important role in chlorination metallurgy, which is divided into solid (NaCl, KCl, CaCl₂, AlCl₃, FeCl₂, FeCl₃, MgCl₂, NH₄Cl, NaClO, NaClO₃) and gas (Cl₂, HCl, CCl₄) [24–29]. Compared with gaseous chlorinating agents, the solid chlorinating agents are easier to handle and more environmentally friendly.

Table 1. Melting temperature, boiling temperature, and sublimation temperature for vanadium compounds.

V-O-Cl Substance	Transition Temperature (°C)
VCl ₂	T _m = 1347
	T _s = 1407
	T _b = 1530
VCl ₃	T _s = 833
VCl ₄	T _b = 151
VOCl ₃	T _b = 127
VO ₂ Cl	T _b = 177
VOCl ₂	T _s = 511
VOCl	T _s = 1120
VO	T _m = 1790
V ₂ O ₃	T _m = 1970
VO ₂	T _m = 1545
V ₂ O ₅	T _m = 690

T_m, melting temperature; T_b, boiling temperature; T_s, sublimation temperature.

The traditional chlorination method of extracting vanadium with NaCl as an additive will produce NaVO₃ and then ammonia nitrogen wastewater will be produced in the process of preparing V₂O₅. The carbochlorination method of extracting vanadium to prepare VOCl₃ will not produce ammonia nitrogen wastewater. Molten salt chlorination of extracting vanadium will obtain VCl₃, and metal V will be obtained by molten salt electrolysis. In this work, these two new processes will be introduced.

2. Vanadium Reserves and the Major Vanadium Producers

Table 2 shows the world's vanadium ore reserves in 2018. More than 99% of the world's vanadium ore reserves are concentrated in China, Russia, South Africa and Australia [30]. Meanwhile, China has the largest vanadium reserves. According to statistics, in 2018, about 16% of the world's vanadium products directly came from vanadium-titanium magnetite, about 68% of the vanadium products came from the vanadium-rich steel slag (and a small amount of phosphorus-rich vanadium slag) obtained by vanadium-titanium magnetite after iron and steel metallurgical processing, and approximately 16% of vanadium products were produced from recovered vanadium-containing by-products (vanadium-containing fuel ash, waste chemical catalysts) and vanadium-containing stone coal [30]. Table 3 shows the overview of major vanadium producers in the world in 2018 [30]. In 2018, the world's total vanadium output calculated in the form of metal vanadium was 91,844 t [30]. The global market share of vanadium products in 2018 was approximately 90.8% ferroalloy products (FeV, VN, ferrovanadium nitride, etc), approximately 4.2% non-ferrous metals such as Ti, and about 5% of vanadium compounds (vanadium oxide, ammonium vanadate, VOSO₄, etc.) for the chemical industry, energy storage and other fields [30]. Like the consumption pattern of the global vanadium market, more than 90% of China's vanadium is used in the steel industry in the form of vanadium alloys [30].

Table 2. Global vanadium ore reserve calculated by metallic vanadium in 2018 (10 kt) [30].

China	Russia	South Africa	Australia	United States	Brazil
950	500	350	210	4.5	13

Table 3. Overview of major vanadium producers in the world in 2018 [30].

Company Name	Production Capacity (V ₂ O ₅)/t	Products	Raw Material
Ansteel Pangang Group Co., Ltd.	40,000	FeV, VN, vanadium oxide, V-Al alloy	Vanadium slag
Russian (Evraz) company	30,000	FeV, vanadium oxide, V-Al alloy, catalyst	Vanadium slag, fly ash, spent catalyst
HBIS Group Chengsteel company	25,000	FeV, VN, ferrovanadium nitride, vanadium oxide	Vanadium slag
Beijing Jianlong Heavy Industry Group Co., Ltd.	15,000	VN, vanadium oxide	Vanadium slag
Austria Treibacher Industrie AG	13,000	V ₂ O ₃ , V ₂ O ₅ , FeV	Vanadium slag
Glencore (Xstrata)	12,000	FeV, vanadium oxide	vanadium-titanium magnetite
Sichuan Chuanwei Group Chengyu Vanadium Titanium Technology Co., Ltd.	12,000	V ₂ O ₅	Vanadium slag
Sichuan Desheng Group Vanadium and Titanium Co., Ltd.	12,000	Vanadium slag	Vanadium slag
Largo Resources Ltd. Brazil	11,000	V ₂ O ₅	Vanadium-titanium magnetite
Maracás Menchen Mine			
Bushveld Vametco, South Africa	6000	VN, vanadium oxide	Vanadium-titanium magnetite
Australia Atlantic Vanadium PTY Ltd.	12,000	FeV, vanadium oxide	Vanadium-titanium magnetite
Vanchem Vanadium Product (Pty) Ltd.	10,000	FeV, vanadium oxide, catalyst	Vanadium-titanium magnetite, vanadium slag
Czech Republic, Germany, Canada, Japan, India, Taiwan, Thailand, etc.	12,000	V ₂ O ₅ , V-Al alloy, FeV, etc.	Slag, waste catalyst, fuel ash, etc.
Other Chinese manufacturers	37,000	V ₂ O ₅ , V-Al alloy, VN, FeV, etc.	Vanadium slag, waste catalyst, stone coal

3. Chlorination Thermodynamics of Vanadium Oxides

Vanadium in vanadium-titanium magnetite, vanadium slag, and stone coal mainly exists in trivalent form. Meanwhile, the V⁵⁺ compounds are the very stable. Thus, V₂O₃ and V₂O₅ were selected as the reactants for thermodynamic calculation by HSC Chemistry 6.4. The possibilities of V₂O₃ reacting with different chlorinating agents are calculated from the thermodynamic viewpoint as shown in Equations (1)–(10). Figure 1 shows the standard Gibbs free energies of reactions between V₂O₃ and chlorination agents at 0–1300 °C. V₂O₃ can be chlorinated to VCl₃ by AlCl₃, CCl₄ and COCl₂. Gibbs free energies of reaction between V₂O₃ and AlCl₃ increases with increasing temperature. Thermodynamically, increasing temperature is not conducive to AlCl₃ chlorination. However, V₂O₃ cannot be chlorinated to VCl₃ by the NaCl, CaCl₂, FeCl₂, FeCl₃, MgCl₂, HCl or Cl₂ at 0–1300 °C.

Figure 1. The standard Gibbs free energies of reactions between V_2O_3 and chlorination agents (reactions 1–10).

The V_2O_5 reacting with different chlorinating agents are as follows: Equations (11)–(20). Figure 2 shows the standard Gibbs free energies of reactions between V_2O_5 and chlorination agents. V_2O_5 can be chlorinated to VOCl_3 by FeCl_3 , AlCl_3 , CCl_4 and COCl_2 at 0–1300 °C. However, V_2O_3 cannot be chlorinated to VOCl_3 by the NaCl , CaCl_2 , FeCl_2 , MgCl_2 , HCl and Cl_2 at 0–1300 °C.

The V_2O_5 and V_2O_3 reacting with C and Cl_2 in the temperature range from 0 °C to 1300 °C are expressed as follows in Equations (21) and (22). Figure 3 shows standard Gibbs free energies of reactions 21–22 at 0–1300 °C. Adding C realizes the chlorination of V_2O_5

and V_2O_3 to $VOCl_3$ by Cl_2 at 0–1300 °C. However, the effect of increasing temperature on the chlorination of V_2O_3 and V_2O_5 is opposite.

Figure 2. The standard Gibbs free energies of reactions between V_2O_5 and chlorination agents (reactions 11–20).

Figure 3. Variation of standard Gibbs free energy of reactions 21–22 with temperature.

Under an oxygen atmosphere, the equations for the NaCl roasting reaction of V_2O_3 and V_2O_5 are as shown in Equations (23) and (24). Figure 4 shows the variation of standard Gibbs free energy of reactions 23–24 with temperature. Under the same conditions, V_2O_3 is more easily chlorinated. Thermodynamically, increasing temperature is not conducive to NaCl chlorination of V_2O_3 . The reaction of V_2O_3 and different chlorinating agents ($FeCl_2$ and $FeCl_3$) are as shown in Equations (25) and (26). It can be seen from Figure 4 that V_2O_3 can be chlorinated by $FeCl_2$ and $FeCl_3$ under an oxygen atmosphere.

Figure 4. Variation of standard Gibbs free energy of reactions 23–26 with temperature.

According to the above thermodynamic analysis, the valence state of vanadium, reaction temperature, atmosphere and chlorinating agent play a very important role in the chlorination of vanadium. Thus, the chlorination of vanadium can be achieved by selecting appropriate conditions. The following will introduce the progress of chlorination of vanadium-containing materials.

4. Application of Chlorination Method

4.1. Chlorination Extraction of Vanadium from Vanadium Titanomagnetite

Vanadium-titanium magnetite is mainly composed of iron (Fe), vanadium (V) and titanium (Ti) elements, which is multi-element symbiotic iron ore containing a small amount of cobalt (Co), nickel (Ni), chromium (Cr), scandium (Sc) and gallium (Ga) [31,32]. The reserves of vanadium-titanium magnetite in the Panzhihua-Xichang regions in China amount to about 9.66 billion tons [33]. The content of vanadium pentoxide in vanadium-titanium magnetite is 0.1 wt%–2 wt% [34]. Jena et al. [23] proposed that under the action of oxygen and water, NaCl as an additive reacts with the vanadium in the vanadium bearing titaniferous magnetite. The roasted samples were leached with hot water. More than 90% of V was extracted. The reaction Equations are as follows in Equations (27)–(31).

To some extent, the presence of SiO_2 and the formation of HCl and Cl_2 can promote the extraction of vanadium [23,35,36]. Zheng et al. [37] first calculated the feasibility of extraction vanadium from vanadium-rich resources with FeCl_2 and FeCl_3 . Thermodynamic calculations show that the higher the valence of vanadium in vanadium titanomagnetite,

the easier it is to extract vanadium. Therefore, the chlorinated atmosphere was selected as the oxygen atmosphere. The reaction Equations are as follows in Equations (32)–(36). Under the optimal experimental conditions (827 °C, reactant (vanadium titanomagnetite)—chlorination agent (FeCl_3) molar ratio of 1:2, 2 h, oxygen atmosphere), the extraction ratio of vanadium is 32%.

Chloride extraction of vanadium from vanadium-titanium magnetite has long been used. However, the content of vanadium in vanadium-titanium magnetite is low, and the cost of directly extracting vanadium in vanadium slag using chlorination method is high. Thus, it is not recommended to extract vanadium directly from vanadium-titanium magnetite by chlorination method.

4.2. Chlorination Extraction of Vanadium from Vanadium Slag

Vanadium slag is produced from vanadium-titanium magnetite by blast furnace smelting and the vanadium extraction process in a converter [38,39]. Vanadium slags contain 30–40 wt% total Fe, 6.9–14.4 wt% TiO_2 , 13.5–19.0 wt% V_2O_3 , 0.9–4.6 wt% Cr_2O_3 , and 7.4–10.7 wt% MnO. The main phases of vanadium slag consist of $(\text{Fe,Mn})(\text{V,Cr})_2\text{O}_4$, $(\text{Fe,Mn})_2\text{SiO}_4$ and Fe_2TiO_4 . According to the phases of vanadium slag, vanadium is present in the form of V^{3+} , from which it is difficult to extract vanadium by direct leaching [40,41].

In order to extract vanadium, the traditional method is to oxidize insoluble low-valent vanadium to soluble high-valent vanadium in aqueous solution [42,43]. Figure 5 shows a flow chart of extracting vanadium from vanadium slag by NaCl roasting. The roasting temperature is about 800 °C. After roasting, vanadium in the solid exists in the form of NaVO_3 , and then dissolves to obtain NaVO_3 solution. Vanadium is precipitated in the form of ammonium vanadate by adding ammonium salt (NH_4Cl , NH_4HCO_3 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$). Ammonium vanadate is calcined to obtain V_2O_5 at about 550 °C. Under the action of oxygen, NaCl as an additive reacts with the vanadium spinel in the vanadium slag. The reaction Equation is as follows in Equation (37). The conversion rate of vanadium can reach 85% [44,45].

Figure 5. Flow chart of extracting vanadium from vanadium slag by NaCl roasting.

A total of 85.8% of V in vanadium slag was extracted by acidic sodium chlorate solution. V^{3+} in vanadium slag was oxidized by $NaClO_3$ as a chlorinating agent. The reaction Equation is as follows in Equation (38) [46].

Sun et al. [47] proposed chlorination of vanadium slag by $FeCl_3$. Under the optimal experimental conditions (827 °C, reactant (vanadium slag)—chlorination agent ($FeCl_3$) molar ratio of 1:2, 2 h, oxygen atmosphere), the extraction ratio of vanadium in vanadium slag is 57%. Du [48] investigated carbochlorination of pre-oxidized vanadium slag. The flow chart of extracting vanadium from vanadium slag by chlorination is shown in Figure 6. The carbochlorination temperature is about 650 °C. Vanadium is volatile in the form of $VOCl_3$. $VOCl_3$ was oxidized to V_2O_5 by O_2 . The equations of the main reactions involved are (39)–(41). The effect of time, temperature, petroleum coke and chlorine pressure fraction were studied. Under optimal process conditions (650 °C, 120 min, $P(Cl_2)/P(Cl_2 + N_2) = 0.5$, 10% of petroleum coke mass fraction), 18.8% of Fe and 87.5% of V were extracted. Wastewater containing high Na^+ and NH_4^+ is scarcely produced in whole process.

Figure 6. Flow chart of extracting vanadium from vanadium slag by carbochlorination.

In order to extract vanadium from vanadium slag, Liu et al. [49–55] proposed to use selective chlorination method to extract vanadium. Because to the existence form and value of valuable metal elements (Fe, Mn, V, Cr and Ti) in vanadium slag, NH_4Cl was selected to chlorinate Fe and Mn in vanadium slag. Thermodynamic calculations show that the iron and manganese in vanadium slag could be chlorinated by hydrogen chloride, but the V, Cr and Ti could not be chlorinated in the temperature range from 0 to 1000 °C. Under optimal chlorination conditions, the chlorination ratio of iron and manganese were 72% and 95%, respectively. Meanwhile, the enrichment ratio of V, Cr and Ti was obtained as 48%. In addition, $AlCl_3$ was selected to chlorinate V, Cr and Ti in vanadium slag. Figure 7 shows a flow chart of extracting vanadium from vanadium slag by $AlCl_3$ chlorination. The chlorination temperature is about 900 °C. Vanadium after chlorination exists in the form of VCl_3 . Metal V was obtained by molten salt electrolysis at 900 °C. The effects of reaction temperature, reaction time, mass ratio of $AlCl_3$ /slag and mass ratio of salt/ $AlCl_3$ on the chlorination ratio of valuable elements were investigated. Under optimal chlorination

conditions (AlCl_3 —slag mass ratio of 1.5:1, (NaCl-KCl)- AlCl_3 mass ratio of 1.66:1, at 900°C , 8 h.), the chlorination ratio of iron, vanadium, chromium and manganese were 90.3%, 76.5%, 81.9% and 97.3%. The volatilization ratio of titanium was 79.9%. The results of kinetic study indicate that the rate-control step of vanadium chlorination process was the surface chemical reaction. The vanadium and chromium in vanadium slag after AlCl_3 chlorination were present in the form of VCl_3 and CrCl_3 in molten salt. The main reaction was as follow (42).

Figure 7. Flow chart of extracting vanadium from vanadium slag by AlCl_3 chlorination.

4.3. Chlorination Extraction of Vanadium from BOF-Slag

The basic oxygen furnace (BOF)-slags contains 31–56% CaO , 10–27% SiO_2 , 1–4.5% Al_2O_3 , 5–35% Fe compounds, and less than 1% of vanadium [56]. Seron et al. investigated the recovery of vanadium from BOF-slugs by oxy-carbochlorination. Under specific conditions (900°C , chlorine partial pressure 0.2, 90 min, 50% carbon content), the recovery ratio of vanadium in slag can reach 95% [57].

4.4. Chlorination Extraction of Vanadium from Stone Coal

Black shale is one of China's most important vanadium resources, accounting for more than 87% of domestic vanadium reserves [58,59]. It is estimated that the reserves of vanadium in the form of V_2O_5 in stone coal are 118 million tons [60]. However, the ordinary grade of vanadium in black shale is usually below 2 wt% [58,59]. In China, vanadium in most of the stone coal replaces trivalent aluminum in mica minerals in a quasi-homogeneous form. The chemical formula of vanadium-containing illite is $\text{K}(\text{Al}, \text{V})_2(\text{OH})_2[\text{Si}_3\text{Al}]\text{O}_{10}$. The mica mineral structure is very stable. It is difficult to destroy the lattice structure by general concentration of acid and alkali. Thus, in order to extract vanadium from vanadium-containing mica, the lattice structure of vanadium containing mica first needs to be destroyed [61].

Under the action of oxygen and water, NaCl as an additive reacts with the pre-decarburized stone coal [62,63]. The reaction Equation is expressed as follow (43):

where m is the number of vanadium ions replacing aluminum ions in hydromica octahedron.

NaCl has a melting point of 801 °C, which tends to keep the structure stable and does not decompose at high temperature. However, due to the presence of V, Al, Fe, and other oxides in the stone coal, NaCl can be decomposed at lower temperature to generate Cl_2 with high chemical reactivity. The reaction is described as follows in Equations (44)–(47). Cl_2 can react with low-valent vanadium to form VOCl_3 , and VOCl_3 is an intermediate product that can be further oxidized to V_2O_5 . The presence of Cl_2 promotes the high temperature roasting to destroy the crystal structure of illite. The oxidation of the exposed trivalent vanadium changes to a higher valence state. Cl_2 is more active than oxygen at high temperature and is more easily adsorbed on the surface of minerals. The promotion of Cl_2 on the oxidation of low-cost vanadium cannot be ignored. Thus, NaCl as an additives agent was selected for extracting vanadium from stone coal [63–66].

The possible chemical reaction between vanadium oxide (V_2O_3 , VO_2 , and V_2O_5) and the solid chlorinating agent (NaCl, CaCl_2 and FeCl_3) was calculated by FactSage 7.1 (Montreal, Canada) using the database of FactPS, FToxid and FT salt. The results show that vanadium oxide cannot be directly chlorinated thermodynamically by NaCl and CaCl_2 as solid chlorinating agents. However, V_2O_4 and V_2O_5 can be chlorinated by FeCl_3 . Meanwhile, V can be separated from black shale by controlled roasting temperature of chlorination volatilization [67]. In the air, the structure of illite and muscovite in stone coal is hard to be destroyed by roasting without additives. Zhang et al. [68] studied that the vanadium-bearing stone coal was roasted in chlorine, and 90% of V in the form of VOCl_3 was extracted at 1000 °C for 1 h. Li et al. [69] investigated extraction of vanadium by leaching. Under the optimal leaching conditions (liquid-to-solid ratio of 2, oxygen partial pressure of 1200 kPa, 90 °C, 6 h, 1.5 g/L NaClO, 15 g/L HF, 100 g/L H_2SO_4), 91% of V in vanadium slag was extracted by NaClO- H_2SO_4 -HF system under atmospheric pressure. V^{3+} in stone was oxidized by NaClO as a chlorinating agent and oxidant.

4.5. Chlorination Extraction of Vanadium from Spent Catalysts

Catalysts are extensively used in sulfuric acid production and petroleum refining [70,71]. More than 100,000 tons of spent hydrosulphurization catalysts are produced every year, which usually contain the valuable elements V, Mo, Ni, and Co [72]. Vanadium in spent catalyst is present in the form of sulfide (V_2S_3 or V_3S_4) [73]. Oxidation roasting of spent catalyst and subsequent NaCl/ H_2O roasting of oxide were proposed by Biswas et al. [74], and 81.9% of V was extracted. The reactions were as follows in Equations (48) and (49):

There are two processes (direct chlorination and roasting chlorination) for recovering vanadium from spent hydrosulphurization catalysts by Cl_2 chlorination.

In addition to metal elements such as vanadium and molybdenum, spent catalysts also contain elemental carbon and sulfur. Direct chlorination of spent catalysts was investigated by Gaballah et al. [75]. In order to recover Mo, V, Ni and Co, Cl_2/N_2 , Cl_2/air , and $\text{Cl}_2/\text{CO}/\text{N}_2$ gas mixtures were used to chloride spent catalysts. Vanadium sulphide was chlorinated to vanadium chloride as expressed in the reaction Equations (50)–(52). A total

of 75% of V in the form of VCl_4 and/or VOCl_3 was recovered by Cl_2 /air gas mixture at less than 600 °C.

Vanadium sulfide in the spent catalyst is first oxidized to oxide at 300–500 °C. Vanadium oxide was chlorinated by Cl_2/N_2 , Cl_2/O_2 , or Cl_2/CO in the temperature range 300 °C to 600 °C. Finally, V was volatilized in the form of VCl_4 or VOCl_3 to achieve separation from other elements (Co, Ni). A total of 65% of V from oxidized V sulfide can be recovered by $\text{Cl}_2/\text{N}_2 = 1$ at 500 °C for 19 h. Meanwhile, V sulfide is directly chlorinated without roasting, and 80% of V can be recovered by $\text{Cl}_2/\text{N}_2 = 1$ at 500 °C for 0.5 h [76].

The affinity of metal to oxide is stronger than that of metal to sulfur. Under the same conditions, sulfides are easier to chlorinate than oxides. Thus, direct chlorination of vanadium sulfide is better than chlorination after oxidation of vanadium sulfide [77].

4.6. Chlorination of V_2O_5

Mink et al. [78] reported that CCl_4 reversibly dissociate and adsorbs on the two exposed vanadium atoms of the basic (001) plane of V_2O_5 before the chlorination reaction. The mechanism of chlorination of V_2O_5 by CCl_4 was analyzed by MS and XPS. Before the formation of the volatile final product VOCl_3 , the surface vanadium atoms gradually acquire two chlorine atoms [79]. The kinetics of chlorination of V_2O_5 by CCl_4 was investigated by Jean et al. [80]. A total of 87% of V_2O_5 could be chlorinated by CCl_4 at 480 °C in 30 min. Chlorination reaction conforms to topochemical reaction model. According to analysis of kinetics results, the following mechanisms, Equations (53)–(58), at different temperatures, were proposed.

a. 280–370 °C

b. 410–515 °C

The whole reaction can be expressed by the following Formula (59)

Gaballah et al. [81] studied kinetics of chlorination of V_2O_5 with Cl_2 -CO- N_2 , Cl_2 - N_2 , and Cl_2 -air gas mixtures. Thermodynamic calculation showed that chlorinated product was mainly VOCl_3 during the Cl_2 chlorination of V_2O_5 . However, VCl_4 may be formed during the carbochlorination of vanadium pentoxide. The results of kinetics indicated that the rate-control step of V_2O_5 chlorination process between 500 °C and 570 °C with Cl_2 - N_2 was a chemical reaction. Pore diffusion and chemical reaction were the limiting

step for the V_2O_5 chlorination in the temperature range of 570 °C to 650 °C. In Cl_2 -CO- N_2 atmosphere, the limiting step of carbochlorination of V_2O_5 at 400–620 °C was the chemical reaction. Brocchi et al. [6] systematically studied the carbon-chlorination of V_2O_5 from thermodynamics between 627 °C and 1327 °C. In carbon-chlorination reaction of V_2O_5 , the most stable vanadium oxychloride and vanadium chloride are $VOCl_3$ and VCl_4 , respectively. E. Mccarley et al. [82] reported a process for preparing high-purity V_2O_5 (maximum of 100 ppm impurities) by carbon chlorination using V red cake (88 wt% of V_2O_5) as raw materials. Pap et al. [83] reported that the chlorination of V_2O_5 by three chlorinating agents (Cl_2 , $COCl_2$ and CCl_4) is compared from the aspects of thermodynamics and kinetics. The results showed that V_2O_5 can be chlorinated thermodynamically by $COCl_2$ and CCl_4 at 127 °C, and the chlorinated products were $VOCl_3$ and CO_2 . However, the reaction of V_2O_5 with Cl_2 can occur obviously when the temperature exceeds 477 °C. The chlorinated product was $VOCl_3$ and O_2 . The chlorination kinetics showed that the apparent activation energy of V_2O_5 chlorinated by Cl_2 , CCl_4 , and $COCl_2$ were 126 kJ/mol, 77 kJ/mol, and 48 kJ/mol, respectively. High-purity V_2O_5 (99.95 wt%) is prepared by chlorinating industrial grade V_2O_5 (96.7 wt%) with $AlCl_3$. The reactions involved are as follows in Equations (60)–(64). Under the protection of purity Ar, the chlorination ratio of V_2O_5 at a $V_2O_5:AlCl_3$ mole ratio of 1:6, 180 °C, and 3.5 h was 62%, and a large amount of $VOCl_3$ was collected. When NaCl is added to the chlorination reaction system, the chlorination ratio of vanadium can reach 83.4% at mole ratio of $AlCl_3:V_2O_5$ of 6:1 and mole fraction of NaCl of 0.6 in the NaCl- $AlCl_3$ system [84,85].

4.7. Chlorination Extraction of Vanadium from Other Vanadium-Containing Materials

Petroleum coke, fly ash and carbonaceous gold ore also contain a certain amount of vanadium. 0.6 Mt/year of petroleum coke was produced from Syrian petroleum refineries. The extraction ratio of vanadium can reach 60% by NaCl-roasting [86]. The vanadium content in fly ash is as low as 1–7%. The fly ash was treated by acid leaching, oxidation of $NaClO_3$, and precipitation [87]. Murase et al. [88] investigated extraction and separation of vanadium from a fly ash of Orimulsion. Air- Cl_2 or N_2 - Cl_2 gas mixture were used to chlorinate valuable elements (V, Ni and Mg). The separation of V and Fe were achieved by controlled temperature of chlorination. V and Fe was selectively extracted by chlorination at 400 °C and 500 °C, respectively. Mg and Ni in residue were extracted by chlorination of N_2 - Cl_2 - Al_2Cl_6 (g) at 600 °C. The extraction and separation of V, Ni and Mg were successfully achieved by the method of chlorination. The content of vanadium in refractory carbonaceous gold ore is 1.1 wt%. Wang et al. [89] investigated extraction and separation of vanadium from carbonaceous gold ore by NaCl roasting. After NaCl roasting, Au volatilizes in the form of $AuCl_3$ and V in the form of $NaVO_3$ remains in the roasted solid. The reactions were as follows in Equations (65)–(69).

The influences of experiment conditions including NaCl dosage, time and temperature were studied. Under optimal process conditions, (air gas flow rate 1 L/min, 4 h, 800 °C, NaCl 10%), the extraction ratios of V and Au are 85.3% and 92%.

4.8. Treatments of Chlor-Containing Compounds in Gas, Solid and Solution

Regarding the Cl₂ and HCl off-gas generated in the chlorination process, the first method is recycling, and the second method is the absorption of alkaline solution. The chloride in the solid can be washed to remove chloride ions. The chlor-containing wastewater can be treated by solvent extraction, the electrochemical method, separation interception method, the principle of precipitation, and ion exchange [90].

5. Conclusions and Outlook

The research progress on the treatment of vanadium-containing materials with various chlorinating agents (solid and gas) is summarized in terms of thermodynamics and kinetics.

The NaCl roasting method is used to treat vanadium titanomagnetite, vanadium slag, stone, spent catalysts, petroleum coke, and carbonaceous gold ore. The NaCl roasting method has the characteristics of short process, less investment and less equipment, etc. In the 1970s, in China, the price of vanadium was very high and hundreds of small-scale vanadium extraction plants adopted the NaCl roasting method to extract vanadium from vanadium-containing materials (stone coal) [63]. However, Cl₂ and HCl generated during the NaCl roasting process makes it highly demanding for the equipment's anti-corrosion performance. The environmental pollution caused by Cl₂ and HCl gas and the threat of Cl₂ and HCl gas to workers' health are also fatal defects of NaCl roasting. Due to increasingly strict environmental protection policies, the NaCl roasting method has become outdated and has gradually been replaced by other roasting methods.

The demand for high-purity vanadium pentoxide is increasing in all-vanadium flow batteries and high-purity metal vanadium. Therefore, efficient preparation of high-purity vanadium pentoxide is urgently needed [91]. Due to the low melting point and boiling point of vanadium chloride, vanadium chloride has a greater advantage than vanadium oxide in separation and enrichment. The advantages of chlorination method in the preparation of high-purity vanadium are very obvious, and it has very good development prospects.

Trivalent vanadium oxide is difficult to leach. Thus, the traditional vanadium extraction method is to oxidize vanadium to pentavalent vanadium for extraction. However, the toxicity of vanadium compounds increases with the increase of vanadium valence, and the pentavalent vanadium compounds are the most toxic. More than 90% of vanadium produced in industry is added to steel in the form of vanadium alloys. Trivalent vanadium oxide can be chlorinated to VCl₃ by AlCl₃. Metal V can be obtained by reduction or electrolysis of VCl₃. Thus, the direct chlorination of low-valent vanadium is also a very promising process.

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