Vanadium sustainability in the context of innovative recycling and sourcing development

M. Petranikova a,⁎, A.H. Tkaczyk b, A. Bartl c, A. Amato d, V. Lapkovskis e, C. Tunsu a

a Chalmers University of Technology, Department of Chemistry and Chemical Engineering, Kemivägen 4, 421 96 Gothenburg, Sweden
b University of Tartu, Institute of Technology, Ravila Street 14a, 50411 Tartu, Estonia
c TU Wien, Institute of Chemical Engineering, Getreidemarkt 9/166, 1090 Vienna, Austria
d Polytechnic University of Marche, Department of Life and Environmental Sciences-DiSVA, Via Brecce Bianche, 60131 Ancona, Italy
e Riga Technical University, Scientific Laboratory of Powder Materials & Institute of Aeronautics, 6B Kipsalas Str, Lab. 110, LV-1048 Riga, Latvia

A R T I C L E   I N F O

Article history:
Received 26 November 2019
Revised 4 April 2020
Accepted 6 April 2020
Available online 13 June 2020

Keywords:
Vanadium
Criticality
Properties
Production
Recycling

A B S T R A C T

This paper addresses the sustainability of vanadium, taking into account the current state-of-the-art related to primary and secondary sources, substitution, production, and market developments. Vanadium plays a critical role in several strategic industrial applications including steel production and probable widespread utilization in next-generation batteries. Confirming the importance of vanadium, the European Commission identified and formally registered this metal on the 2017 list of Critical Raw Materials for the European Union. The United States and Canada have also addressed the importance of this metal. Like the European economy, the American and Canadian economies rely on vanadium and are not globally independent. This recognized importance of vanadium is driving many efforts in academia and industry to develop technologies for the utilization of secondary vanadium resources using hydrometallurgical and pyrometallurgical techniques. In this paper, current efforts and their outcomes are summarized along with the most recent patents for vanadium recovery.

© 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Contents

1. Introduction ........................................................................................................... 522
2. Criticality, sources ................................................................................................. 522
  2.1. Occurrence ......................................................................................................... 522
  2.2. Vanadium in the EU ......................................................................................... 523
  2.3. Markets ............................................................................................................. 525
  2.4. Mining ............................................................................................................... 525
  2.5. Reserves ........................................................................................................... 526
  2.6. Substitution ...................................................................................................... 527
3. Price, market development ..................................................................................... 528
4. Properties and applications; future trends ............................................................. 528
5. Production (ways, industrial processes, companies, etc.) ...................................... 530
6. Recycling ................................................................................................................ 531
  6.1. Roasting and leaching of vanadium from the secondary sources ...................... 531
  6.2. Recovery of vanadium using solvent extraction ............................................... 533
  6.3. Recovery of vanadium using ion exchange ...................................................... 534
  6.4. Pyrometallurgical processing of vanadium-containing sources ...................... 534
7. The study of technological innovation change ....................................................... 536
8. Discussion .............................................................................................................. 539
Acknowledgements ................................................................................................. 539
References ............................................................................................................... 540

⁎ Corresponding author.
E-mail address: martina.petranikova@chalmers.se (M. Petranikova).

https://doi.org/10.1016/j.wasman.2020.04.007
0956-053X/C2020 The Author(s). Published by Elsevier Ltd.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
1. Introduction

Metals are essential materials of strategic importance, as they support the technologies which are ubiquitous in the modern world. To meet the intensifying demands of today’s technologically advanced society, modern industrial applications are increasing the quantity, diversity, and quality of metals in their products.

The European Commission (EC) has recognized that the economies of individual countries as well as the European Union (EU) as a whole are highly influenced by access to raw materials and metals resources (EC, 2017a). The strategic importance of vanadium (V) is reflected by its presence in the list of 27 critical raw materials issued by the European Commission (EC, 2017a). The list represents a selection of the metals of high importance for the EU economy, which possess a high risk of the supply. The United States and Canada have also addressed the importance of raw materials. Like the European economy, the American and Canadian economies rely on vanadium and are not globally independent; vanadium is supplied from international sources and the utilization of secondary sources (petroleum residues, spent catalysts, utility ash, and vanadium-bearing pig iron slag) (Polyak, 2019).

Vanadium plays a critical role in several industrial applications, especially in steel production. Vanadium, when added in small amounts to certain ferrous alloys, can significantly improve alloy properties and performance. Moreover, specific attributes of vanadium are utilized for the production new generation batteries which support the inclusion of renewable sources of electricity on the electric grid. Thus vanadium, in addition to its conventional application, plays a very significant role in the decarbonization of the energy industry. Countries can make risk-informed decisions based on a sustainability assessment of vanadium, based on comparing the demand and supply from primary and secondary sources.

Considering the strategic international relevance of vanadium and the strong interest for both the market and the scientific community, a comprehensive overview of the current state-of-the-art is essential to identify the worldwide situation and to accurately assess risks. In this regard, some recent literature has addressed the vanadium issue, but the work has concentrated on specific aspects: the processes of extraction and recovery of vanadium from several matrices (primary or secondary resources) (Gilligan and Nikoloski, 2020; Le and Lee, 2020; Peng 2019; Zhang et al. 2014); combinations of vanadium with other elements (Akcil et al., 2015; Ferella, 2020; Seredkin et al., 2016); the effects of vanadium on the environment and human health (Domingo 1996; Imtiaz et al., 2015; Gummow, 2011; Watt et al., 2018); and the biological role of vanadium (Rehder, 2015). Some literature has described possible applications of vanadium in different technologies, mainly batteries (Choi et al., 2017; Gonçalves et al., 2020; Lourenssen et al., 2019; Shi et al. 2019; Skyllas-Kazacos et al., 2016; Parasuraman et al., 2013; Xu et al., 2020). Nearly two decades ago, authors Moskalyk and Alfantazi developed an overview of vanadium based on prevailing technological conditions at that time (Moskalyk and Alfantazi, 2003). In this context, the current paper comprehensively addresses the sustainability of vanadium, taking into account the modern state-of-the-art, complementing and expanding upon previous efforts to address important gaps, including attention to the main characteristics that make vanadium strategically essential in today’s technologically-advanced society, as confirmed by market economic trends. In this the present work, the full life cycle of vanadium has been considered, from metal mining to the recovery from waste, and in the context of possible applications. The further focus on the available patents and the funded projects for vanadium recovery provides insight into technological innovation changes, which can be useful in predicting future developments of vanadium sustainability.

2. Criticality, sources

2.1. Occurrence

In the earth’s crust vanadium is a rather abundant element. It shows a concentration of just under 100 ppm in the upper continental crust / earth’s crust which is much higher than most of the other critical elements (Rudnick and Gao, 2003; Yaroshevsky, 2006) as shown in Table 1. Table 1 also demonstrates that the vanadium concentration in seawater is 2 mg/m³ and thus again significantly higher than other critical elements (Haraguchi et al., 2003). Assuming a total volume of earth’s seas of about 1.34x10⁹ km³, approximately 3.10⁹ t vanadium are present in seawater. This is much higher than the known reserves in deposits but nevertheless it is too diluted to make extraction economically viable. Table 1 further outlines that the supply risk as proposed by the EU commission (EC, 2017a) is not directly linked to the concentration of the elements. It is, however, not clear whether vanadium may be an essential element for the human body (Prashanth et al., 2015).

Vanadium deposits may occur in four principal types (Kelley et al., 2017): vanadiferous titanomagnetite deposits; sandstone-
Table 2
Selection of important vanadium minerals (Kelley et al., 2017; Bauer et al., 2017).

| Mineral          | Formula                        | Oxidation state | Vanadium oxide content % | Deposits                                      | Reference                  |
|------------------|--------------------------------|-----------------|--------------------------|-----------------------------------------------|----------------------------|
| Carnotite        | K₂(UO₂)₂(V₂O₈) + 1 – 3H₂O     | 5+              | About 20                 | USA (Colorado, Utah, New Mexico, Arizona), Australia, Kyrgyzstan | Anonymous, 2001-2005a      |
| Coffinite        | U(SO₄)₂[Cr(VO₄)₃]₆H₂O         | 5+              | About 3                  | USA (Colorado, New Mexico, Utah), Germany, Austria, Czech Republic, UK | Anonymous, 2001-2005b      |
| Corvusite        | (Na₂CaK)₆(VO₄)₆(V₂O₈) + 4Fe⁺₂⁺ ₄H₂O (x = 0.8 to 1.2) | 4+, 5+          | 75–85                    | USA (Utah, Colorado, Arizona), Gabon, Kazakhstan | Anonymous, 2001-2005c      |
| Descoizite       | Pb₂Zn(VO₄)₂(OH)₂              | 5+              | About 23                 | Argentina, Mexico, USA (Arizona, New Mexico, Nevada), Namibia, Zambia, Congo Republic, Iran, Austria, Slovenia, Portugal | Anonymous, 2001-2005d      |
| Dolerite         | H₃V₂O₇              | 4+, 5+          | 78–87                    | USA (Colorado, Utah, New Mexico, Arizona, Wyoming), Australia, Argentina | Anonymous, 2001-2005e      |
| Francevillite    | (Ba₂Pb)(UO₂)₂(V₂O₄) + 9H₂O   | 5+              | About 19                 | Gabon, Congo, Zimbabwe, France, Germany, England, Kyrgyzstan, Canada, USA (Pennsylvania) | Anonymous, 2001-2005f      |
| Hewettite        | CaV₂O₇ + 9H₂O               | 4+, 5+          | About 71                 | Peru, USA (Colorado, Utah, Arizona, Nevada, South Dakota, Arkansas), Kazakhstan | Anonymous, 2001-2005g      |
| Montroseite      | (V²⁺,Fe³⁺,V⁴⁺)O(OH)₄        | 3+, 4+          | 10–90                    | USA (Colorado, Utah, Arizona, New Mexico, South Dakota), Czech Republic, Argentina, Gabon, China | Anonymous, 2001-2005h      |
| Mottramite       | Pb₂Cu₂V₂O₇(OH)₅             | 5+              | 21 – 22                  | England, USA (Arizona, New Mexico, Nevada), Chile, Namibia, Zambia | Anonymous, 2001-2005i      |
| Paramontroseite  | VO₂                        | 4+              | 67–73                    | USA (Colorado, Utah, Arizona, New Mexico, South Dakota), Czech Republic, Argentina, Gabon | Anonymous, 2001-2005j      |
| Pascoite         | CaV₂O₇ + 17H₂O              | 4+ or 5+        | 65–66                    | Peru Argentina, USA (Colorado, Arizona, New Mexico) | Peru | Anonymous, 2001-2005k |
| Patronite        | VS₄ or V⁴⁺(OH)₄            | 4+              | 28⁺                      | Peru Argentina, USA (California, Colorado, Oregon, Arizona, Nevada), Japan, Australia, Fiji Islands, Czech Republic, Gabon, Kyrgyzstan, England, USA (Mexico, Colorado, Utah, Arizona, Nevada), Mexico, Argentina, Israel | Anonymous, 2001-2005n |
| Roscoeite        | K⁺V⁴⁺⁺Al²⁺Mg₂Al₅O₁₀(OH)₂½H₂O | 3+              | About 20                 | USA (California, Colorado, Oregon, Arizona, Nevada), Japan, Australia, Fiji Islands, Czech Republic, Gabon | Anonymous, 2001-2005m      |
| Tuyuyumite       | Ca₂(OVO₄)₂ + 8H₂O           | 5+              | About 19                 | Kyrgyzstan, England, USA (Mexico, Colorado, Utah, Arizona, Nevada), Mexico, Argentina, Israel | Anonymous, 2001-2005n      |
| Vanadinite       | Pb₂(VO₄)₂Cl                  | 5+              | About 19                 | Mexico, USA (Arizona, New Mexico), Morocco, Turkey, Namibia, Australia | Anonymous, 2001-2005o      |

* V content (Machatschki, 2013).

hosted vanadium deposits; shale-hosted deposits; vanadate deposits. Vanadiferous titanomagnetite deposits are the most important source for vanadium and deposits can be found all over the world (Kelley et al., 2017). They are usually associated with mafic igneous rocks (e.g. gabbro or anorthosite) found in South Africa, Sweden, Finland or the USA (Fischer, 1975). The most important ore minerals are magnetite (Fe₃O₄) and hematite (Fe₂O₃) but also in rutile (TiO₂) and perovskite (CaTiO₃) deposits are possible sources (Fischer, 1975). Usually vanadium in titaniferous magnetite deposits is concentrated as a solid solution in magnetite-ulvospinel, where V⁴⁺ has replaced Fe³⁺ (Fischer, 1975). Table 2 shows some important minerals for vanadium extraction. Vanadium is also available as a by-product from production processes such as iron and steel, uranium, alumina, phosphorus or lead and zinc (Bauer et al., 2017). It has also to be mentioned that vanadium occurs in fossil fuels such as petroleum, coal, tar sand and oil shale (Breit, 1992).

2.2. Vanadium in the EU

Vanadium has entered criticality in 2017, whereas it was not considered critical in the 2011 (EC, 2011) and 2014 (EC, 2014b) assessment of the EU. According to the latest EU criticality assessment in 2017 the economic importance score (EI) is 3.7 (threshold 2.8) and the supply risk (SR) 1.6 (threshold 1.0) (EC, 2014a). Fig. 1 shows a plot of the materials which have been accessed by the EU in 2011, 2014 and 2017. Vanadium already showed a very high economic importance in 2011 and 2014 but the supply risk was not high enough that the material had to be considered critical. The 2017 plot cannot be directly compared to 2014 and 2011 as the methodology in the 2017 assessment for both the calculations of economic importance and supply risk are now different. However, it is obvious that the relative position (V close to Cr, Mn and Zn in 2011 and 2014) changed tremendously. The economic importance decreased, and the supply risk increased, as a matter of fact vanadium crossed the threshold value and moved into criticality.

Table 3 demonstrates that there is no vanadium extraction in the EU at all (EC, 2017). In the period 2010–2014 the EU imported on average 9124 t vanadium per year (EC, 2017). It is also reported that about 1650 t of vanadium pentoxide is produced in the EU, whereas Belgium, United Kingdom, the Netherlands and Germany are the main producers. Furthermore, 2000 t of ferrovanadium have been produced inside the EU, mainly in the Czech Republic (EC, 2017). Table 3 summarized the available data on vanadium processing according to (EC, 2017).

The British Geological Survey (Brown, 2016) reports imports and exports of vanadium in detail. Table 4 summarizes EU’s imports in 2014 structured according to the product groups of vanadiferous residues, pentoxides and metal (i.e. ferrovanadium). It is striking that for the largest volume of imports vanadiferous residues (46,000 t) are responsible and that these imports exclusively go to Austria. It is, however, likely that the volume of 46,000 t designates the total volume of the material and is not related to the vanadium content. According to the data of the BGS (Brown, 2016) the EU imported a total of about 16,000 t of vanadium pentoxides which is higher than the overall EU imports (9124 t) considered by the EU commission (EC, 2017). Again, the difference could be that the EU commission considers the vanadium content of pentoxide and not the total mass. A volume of 16,000 t (Brown, 2016) of V₂O₅ corresponds to 8960 t vanadium which is in good agreement with 9124 t (EC, 2017). Table 4 also shows that EU’s imports of vanadium metal (i.e. ferrovanadium) is as low as 645 t (Brown, 2016). It is, furthermore, again not clear if the total mass of ferrovanadium or the vanadium content is con-
sidered. Ferrovanadium (e.g. FeV40, FeV60, FeV80) can show vanadium contents between 35 and 85 mass % (EC, 2017). It is not surprising, that the main importers of vanadium to the EU are the main producers (see chapter 2.4), even if the share is not the same. In the period 2010–2014, Russia was the most important supplier for EU’s vanadium and held a share of 71% followed by China and South Africa with a share of 13% each (EC, 2017b).

Table 5 summarizes the exports of vanadium from the EU to third countries (Brown, 2016). The exports of pentoxide (419 t) are much smaller than compared to the imports (16,000 t) which is based on the fact that the material is used for production of vanadium products such as ferrovanadium or vanadium bearing steel alloys. Imports (645 t) and exports (846 t) of ferrovanadium are both on a low level and almost balance each other out.

The question arises, why for Austria a large amount of vanadium imports but not exports are reported. It is known that the Austrian company “Treibacher Industrie AG” treats end-of-life catalysts or production residues containing molybdenum, nickel and vanadium via a pyrometallurgy process by which vanadium is con-

![Fig. 1. EU criticality assessment of 2011, 2014 and 2017 (EC, 2011, 2014b, 2017b).](image-url)
Vanadium is mainly used as alloying element for steel. As demonstrated by Table 6 different categories of steel alloys dominate the vanadium market and shows a share of 90%. The only other applications are titanium alloys, chemicals and other (mainly batteries).

Vanadium serves the purpose to improve the resistance to wear and deformation of steel. Vanadium-containing alloys are used for the hull of submarines, in structural parts, engines and landing gear, but also in gun alloy elements, armour, fuselages and wings, in the field of aeronautics and naval (Moss et al., 2011).

2.4. Mining

The world mining production is plotted in Fig. 2. From 1912 to 1960 production of vanadium was quite low and did not exceed 5000 t. A significant increase occurred between 1960 and 1980 when mine production jumped from 5000 to 38,000 t. Over the next 20 years production stagnated, and it was not until 2000 (41,000 t) that the value of 1980 was further increasing. Since 2000 a strong, near linear growth took place and mine production doubled until 2014. Since then vanadium production has reached a plateau at between 70,000 and 80,000 t (Polyak, 2017, 2018, 2019; Survey, 2016).

World mine production is concentrated in a few countries only. As demonstrated by the charts in Fig. 3, China, Russia and South Africa are the major producers. In 2000 and 2008 no other country held a relevant share of mine production. For 2012 a small production of 272 t was reported for the USA (Polyak, 2014) which accounts less than 0.4% of worldwide production. Starting in 2014 Brazil entered the market and in 2016 the country produced 8400 t (Polyak, 2018). This volume is much smaller as compared to China (45,000 t) Russia (16,000 t) and South Africa (10,000 t) but represents a share of 10%. However, it is obvious that vanadium production is concentrated in a small number of countries only and there is no own production within the EU.

2.3. Markets

Vanadium is mainly used as alloying element for steel. As demonstrated by Table 6 different categories of steel alloys dominate the vanadium market and shows a share of 90%. The only other applications are titanium alloys, chemicals and other (mainly batteries).

Vanadium serves the purpose to improve the resistance to wear and deformation of steel. Vanadium-containing alloys are used for the hull of submarines, in structural parts, engines and landing gear, but also in gun alloy elements, armour, fuselages and wings, in the field of aeronautics and naval (Moss et al., 2011).
Despite this difference it is clear that the mine production is concentrated in three countries only, China, Russia and South Africa.

2.5. Reserves

The volume of extracted material is quite easy to measure. In contrast, it is difficult to estimate the amount of material that can be mined in the future. The USGS gives a classification of reserves for minerals (Menard, 1976) which is briefly summarized in Table 8.

The reserves of vanadium are basically located in the same countries in which relevant mine production takes place. Fig. 4 plots the distribution of the reserves in different countries as reported for 2000, 2008, 2012 and 2016. The share of Russia decreased from 50% in 2000 to 25% in 2016 whereas the share of China increased from 20% in 2000 to 45% in 2016. In 2016 new reserves located in Australia have been reported by the USGS.

As demonstrated by Fig. 5 reserves are not fixed but due to changing market prices, improved mining technologies, depletion of mines or identification of new resources can undergo changes over time. From 1994 to 2018 the resources reported by the USGS doubled from 10 to 20 million t as sketched in Fig. 5. The chart also plots the time to depletion as calculated by Eq. (2.5.1).

\[
\text{Time to depletion } a = \frac{\text{Reserves } t}{\text{Mine production } H} \tag{2.5.1}
\]

Between 1994 and 2018 the time to depletion was decreasing. As the mine production was increasing distinctly (Fig. 2), the time...
to depletion decreased from about 300 years (1994) to about 180 years (2014). It is, however, clear that our economy will not run out of vanadium in the near future. As already discussed the criticality of vanadium is not based on scarcity (Table 1) but on the concentration of mine production in a very few countries (Fig. 3).

2.6. Substitution

According to the EU assessment in 2017 the substitution index for supply risk is 0.94 and the substitution Index for economic importance is 0.91 (EC, 2017b). Both values indicate that substitution is difficult and that the material is more or less irreplaceable in most application. Table 9 shows possible substitutes according to the literature. A closer inspection (Table 10) of the suggested substitute elements (Mn, Mo, Nb, Ti, W) reveal that it will most likely not work in practice. Niobium and tungsten are critical itself and it will make no sense to substitute a CRM by another CRM. Manganese is not considered critical but also inadequate for substitution. Even if the prices for Mn (2000 €/t) are much cheaper than for ferrovanadium (83,810 €/t), the production volume is by far too low. The annual production of manganese is only 20% of vanadium. Even a partial substitution of vanadium by Mn would upset the markets and exceed the production capacities. Regarding the volumes and prices molybdenum and titanium could be a candidate for a vanadium substitute. It is, however, clear that performance of quality by the substitutes in the final products might lag behind. It has to be considered that significant technical adjust-

| Table 8 |
|---|
| **Short summary of reserve classification for minerals according to USGS (Menard, 1976).** |
| | **Term** |
| **Resource** | A concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth’s crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible |
| **Identified Resources** | Resources whose location, grade, quality, and quantity are known or estimated from specific geologic evidence |
| **Reserve Base** | Part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices |
| **Reserves** | That part of the reserve base which could be economically extracted or produced at the time of determination. The term reserves need not signify that extraction facilities are in place and operative. |

Fig. 4. World mine production of vanadium by country in 1,000 t and share in %; data retrieved from: 2000 (Reese, 2002); 2008 (Polyak, 2010); 2012 (Polyak, 2014); 2016 (Polyak, 2018).

Fig. 5. Reserves of vanadium reported for the period 1994 to 2017 (Hilliard, 1996, 1997; Magyar, 2003, 2004, 2005, 2006, 2007, 2008, 2009; Polyak, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019; Reese, 1998, 1999, 2000, 2001, 2002) and estimation for 2018 (Polyak, 2019) compared to the mine production of the respective year; calculation of time to depletion according to Eq. 2.5.1.
ments would be required in order to meet product specifications (2017). Vanadium cannot be replaced in aerospace applications as the strength-to-weight ratio of vanadium-titanium alloys cannot be reached by other materials (2017).

Since the main share of vanadium goes into steel alloys (Table 6), the substitution of vanadium in other markets is less relevant. Titanium is a substitute for vanadium use in paints and varnishes, a specific part of the chemical applications of vanadium. Batteries using vanadium are based on the redox flow technology which is quite new in the market. It is expected that the volume of this battery will grow in the future (Johnson, 2019). Vanadium is, however, the most promising candidate for redox flow batteries (Cunha et al., 2015) and an increasing demand for vanadium from this sector is very likely.

3. Price, market development

As V₂O₅ is the most relevant intermediate it is commonly used as price indicator. Fig. 6 plots the price for vanadium pentoxide in the period from 1910 to 2015. There has been a quite constant ascent from 1910 (1 US$/kg) to 1970 (5 US$/kg) without any significant fluctuations. Starting in 1970 massive price movements occurred, in particular with peaks in 1989 (24 US$/kg) and in 1998 (22 US$/kg), whereas in 2001/2002 the price level of 1970 was reached again (5 US$/kg). Since then a true price rally could be observed. In 2005 the all-time high with 64 US$/kg was reached followed by another peak in 2008 (51 US$/kg). However, since then the price dropped down to 16 US$/kg in 2015.

Fig. 7 plots the price for vanadium pentoxide and ferrovanadium from January 2000 to March 2019. As already plotted in Fig. 6, both products show a distinct price peak in 2005 and 2008. In the period from 2009 to 2017, prices remained rather constant. The situation changed tremendously in 2017. Prices for pentoxide and ferrovanadium increased with a peak in October 2018 (Ferrovanadium: 127 US$/kg) and November 2018 (vanadium pentoxide: 113 US$/kg). However, the prices dropped again and in the first quarter of 2019 prices stabilized at about 75 US$/kg (FeV) and 40 US$/kg (V₂O₅) (Vanadiumprice.com, 2019).

4. Properties and applications; future trends

Vanadium is one of the group five elements, and has two naturally occurring isotopes: ⁵¹V (stable, 99.75% abundance) and ⁵⁰V (t₁/₂ = 1.7*10¹⁷ years, 0.25% abundance) (Greenwood and Earnshaw, 1997). It is shiny, silvery metal with typical metallic bcc structure; it is soft and ductile in its very pure form but

### Table 9
Possible substitutes for vanadium according to USGS (Polyak, 2019) and EU (EC, 2017a).

| Application          | USGS                                      | EU                                      |
|----------------------|-------------------------------------------|-----------------------------------------|
| Steel                | Mn, Mo, Nb, Ti and W to some degree       | Mn, Mo, Nb, Ti and W to some extent     |
| Catalysts            | Pt and Ni can replace V-compounds         | Pt and Ni can replace vanadium compounds|
| Paints and varnishes | No information                            | Ti                                      |
| Batteries            | No information                            | Materials from the alkaline group       |
| Aerospace Ti alloys  | No acceptable substitute                   |                                         |

### Table 10
Basic data for vanadium and possible candidates for substitution.

| Substitute      | Critical | EI² | SR² | Mine production in 2017 [t] | Price [US$/t]³ |
|-----------------|----------|-----|-----|----------------------------|----------------|
| Vanadium        | Yes      | 3.7 | 1.6 | 71,200 (Polyak, 2019)      | 83,810         |
| Manganese       | No       | 6.1 | 0.9 | 17,300 (Corathers, 2019)   | 2060           |
| Molybdenum      | No       | 5.3 | 0.9 | 297,000 (Polyak, 2019)     | 16,006         |
| Niobium         | Yes      | 4.8 | 3.1 | 69,100 (Padilla, 2019)     | 42,280         |
| Titanium        | No       | 4.4 | 0.4 | 181,000 (Bedinger, 2019)   | 4800           |
| Tungsten        | Yes      | 7.3 | 1.8 | 82,100 (Shedd, 2019)       | 30,300         |

¹ (EC, 2017a).
² average price in 2018 according to (Metalary, 2019a, b, c, d, e).
³ average price for ferrovanadium (80%) in 2018 according to (Vanadiumprice.com, 2019).
becomes harder and more brittle when impure. Similar to other members of its group, niobium and tantalum, vanadium has high resistance to corrosion. This is due to the formation of protective oxide films on its surface. Vanadium exhibits oxidation states from +2 to +5, the most stable one being +5 (e.g., V2O5). These include the vanadyl ion VO2+ , one of the most stable diatomic ions known. High temperatures are required for chemical reactions with most non-metals. Vanadium is attacked by hot concentrated mineral acids and is resistant to fused alkali. When it comes to the +5 state, vanadium forms a pentahalide with fluorine. With other non-metals, such compounds are based on oxhalides and pentoxides. Vanadium pentoxide (V2O5) is the final product upon heating with excess oxygen but lower oxides can also form, e.g., VO2, V2O3 or VO. Upon thermal treatment, V2O5 loses oxygen reversibly, making it a versatile catalyst. Industrial applications include the oxidation of SO2 to SO3 for production of sulfuric acid, and the air oxidation or hydrogen reduction of organic compounds, e.g., oxidizer for the production of maleic anhydride. Notable advantage for using V2O5 instead of platinum catalyst include reduced costs, and reduced impurity poisoning, e.g., arsenic (Greenwood and Earnshaw, 1997). For sulfuric acid production, sulfur is oxidized from +4 to +6 and vanadium is reduced from +5 to +4 (Eq. (4.1)); the pentoxide catalyst is regenerated by oxidation with air (Eq. (4.2)).

\[
\begin{align*}
V_2O_5 + SO_2 & \rightarrow 2 VO_2 + SO_3 \\
\text{VO}_2 + O_2 & \rightarrow 2 V_2O_5
\end{align*}
\]

In aqueous solutions, vanadium can form a wide range of oxyanions, depending on pH and concentration. Orthovanadate VO43− , which forms at high pH, is important for crystallographic investigations of phosphoryl transfer enzymes (Davies and Hol, 2004), and is a powerful competitive inhibitor of purified alkaline phosphatase from human liver, intestine and kidney (Seargeant and Stinson, 1979). Phosphate and vanadate compete for the same binding site on the enzyme. The inhibition is reversible, and full enzymic activity can be restored in the presence of adrenaline. The decavanadate ion predominates at lower pH (pH 2–4) and can form from orthovanadate via condensation (Eq. (4.3)).

\[
\text{VO}^{3−} + 24H^+ \rightarrow V_{10}O_{28}^{6−} + 12 H_2O
\]

Potential applications in catalysis have led to studying reduced polyvanadates containing a wide range of vanadium (V) and (IV) ratios, e.g., decavanadates (Soghomonian et al., 1993) or octodecavanadates (Müller et al., 1990). The latter is able to encapsulate negatively charged ions and ions with significantly different radii. Higher nucleicarities have been attained, e.g., \( K_{10}(V_xO_{2y})^{[(x-20)H_2O]} \) (Müller et al., 1991). The studies of such mixed valence species are important not only in catalysis but also geochemistry and, most importantly, biochemistry. The VO4 unit in aforementioned polyvanadates resembles Fe4+ in biochemical systems. This can provide models for biological systems, e.g., incorporation of VO2+ into the biological iron transport, and storage proteins transferrin and ferritin, which have important implications in medicine (e.g., rheumatic arthritis). While vanadium is a versatile catalyst, its predominant application is in the iron and steel industry, as hardening and strengthening agent (Table 11).

Vanadium interacts with carbon present in steel, and forms stable carbides, which strengthen the alloy. Addition of vanadium to steel provides good castability, rollability, reduced roll wear, relative insensitivity to finish rolling temperatures in structural steels, good weldability of structural steels, and protection against oxidation via formation of a protective surface oxide layer (EC, 2011). The amounts used vary from subpercentage up to several percent vanadium (e.g., 5%). The latter is used in high speed steel with high hardness and abrasion resistance, e.g., for power-saw blades and drill bits. In the beginning of the 2000 s, it was estimated that vanadium consumption in the iron and steel sector amounted to 85% of the vanadium-containing products produced worldwide (Moskalik and Alfanzati, 2003). More recent reports put this at 90% and conclude that future demand is expected to increase if the steel demand experiences steady growth (EC, 2011). Vanadium is also used together with aluminum, chromium, iron, nickel, titanium and others in various alloys. The different formulations serve diverse purposes, from common ones such as train rails to specific alloys for aerospace use. Alloys with titanium and aluminum have applications in jet engines and highspeed airframes (EC, 2011), and, currently, there is no substitute for vanadium in aerospace titanium alloys (Moskalik and Alfanzati, 2003). In combination with dysprosium and other elements, vanadium is used in laser materials. It was forecasted that vanadium will play an important role in carbon capture and storage technologies. The main use is high specification steel alloys, e.g., for pipelines. Modelling the future metal demands for carbon capture and storage applications showed that vanadium may have the largest metal requirements as a percentage of current world supply in 2030 (1.3%). Other applications of vanadium include colour modifiers in mercury vapor lamps, target material for X-rays, photographic developer, drying agent in various paints and varnishes, production of pesticides and black dyes (mordants), inks and pigments used in ceramics, printing and textile industries (Moskalik and Alfanzati, 2003). Its non-metallurgical use is predicted to rise due to applications of vanadium in batteries (EC, 2011). Lithium-vanadium phosphates can function well as cathodic material in lithium ion batteries, and gives good cyclability, high voltage and capacity (Nitta et al., 2015). Li3V2(PO4)3 has one of the highest voltage and highest energy cathode identified for lithium ion batteries (EC, 2011). Other energy-related applications include vanadium redox batteries, which exploit the different oxidation states of vanadium (Alotto et al., 2014). Various systems were investigated, e.g., magnesium-vanadium, vanadium-cerium and vanadium-polyhalide but the most promising commercial technology is VRB (vanadium/vanadium redox battery), e.g., vanadium/vanadium dissolved in aqueous sulfuric acid. This system uses the same metal ions in the electrolyte, electrodes and membrane. This prevents cross-contamination, which positively affects the cell capacity in time, and allows for longer lifetime of the battery. During charging, VO2+ ions are oxidized to VO2+ ions (Eq. (4.4)); at the negative electrode V3+ ions are reduced to V2+ ions (Eq. (4.5)). The electrical neutrality of the electrolytes is maintained by movement of protons through a membrane. This gives an open circuit voltage of 1.4 V per cell at 25 °C.

\[
\begin{align*}
\text{VO}^{2+} + H_2O & \rightarrow \text{VO}^{2+} + 2H^+ + e^- \quad \text{(charging)} \\
\text{V}^3+ + e^- & \rightarrow \text{V}^2+ \quad \text{(charging)}
\end{align*}
\]

### Table 11

| Application | Share | Application | Share |
|-------------|-------|-------------|-------|
| Chemical applications, e.g., catalysts for sulfuric acid and maleic anhydride production | 5% | Steel: full alloy | 25% |
| Steel: carbon | 12% | Steel: high strength low alloy | 36% |
| Steel: tools/stainless | 18% | Non-ferrous alloys | 4% |
Vanadium-bromine (V-Br) cells and hybrid vanadium-oxygen redox fuel cells (VOFC) are other applications for energy storing for which vanadium is needed. The VRB technology has been successfully tested, with applications mainly in Asia (Japan) but also South Africa and Europe, and commercial exploitation is ongoing (Alotto et al., 2014). Due to their bulkiness, vanadium batteries are best suited for grid storage.

5. Production (ways, industrial processes, companies, etc.)

Primary sources of vanadium include ore feedstock, concentrates, metallurgical slags and petroleum residues (Moskalyk and Alfantazi, 2003). A significant amount of vanadium is also recycled. According to a recent report, the end-of-life recycling input rate of vanadium in the European Union amounts to 44%, the highest contribution of recycling to meet the Union’s demand of critical raw materials (EC, 2019). Two main types of secondary streams are targeted for recycling: steel scrap, which is recycled along with the vanadium content, and spent catalysts. Vanadium can be recovered and refined via several processes, e.g., calcium reduction, roasting and leaching, solvent extraction and ion exchange (Moskalyk and Alfantazi, 2003). Final commercial products are vanadium metal, ferrovanadium (iron-vanadium alloy), vanadium pentoxide but also various vanadium compounds, depending on the desired application. The main ore feedstock to recover metallic vanadium is titaniferous magnetites. Vanadium and vanadium compounds can also be recovered as by-products in several industrial operations (Moskalyk and Alfantazi, 2003). Such operations include recovery of aluminum and magnesium metal from smelters and refineries, and production of uranium. For the last one, the vanadium left in the raffinate after the solvent extraction of uranium from ore leachate is extracted to an organic phase in a subsequent solvent extraction step, back-extracted with sodium carbonate solution, and precipitated with ammonium sulphate as ammonium metavanadate. This is finally calcined to produce vanadium pentoxide. Other commercial processes, e.g., lead and zinc production in Namibia, processing of iron ore deposits in Finland and Norway (operations stopped during the 1980s), and processing of bauxite residues in France also generated vanadium by-products. Typical processing of primary vanadium-bearing materials involved crushing and roasting with sodium chloride or sodium carbonate at 850 °C, which forms water-soluble sodium metavanadate. After leaching with water, a polyvanadate (red cake) is precipitated with sulfuric acid at pH 2–3. This is heated at 700 °C to produce black, technical grade vanadium pentoxide. Reduction is carried out to obtain vanadium metal (Fig. 8). Pure metal can be obtained via reduction of vanadium pentachloride with hydrogen or magnesium, reduction of vanadium pentoxide with aluminum or calcium, or electrolysis of partly refined vanadium in fused alkali metal halides (Greenwood and Earnshaw, 1997; Moskalyk and Alfantazi, 2003). Vanadium-aluminum alloys can be refined using molten salt electrolysis. Carbon is not preferred for reduction to avoid formation of vanadium carbides. Because the vast majority of vanadium is used in the steel industry as additive (as presented in section 4), ferrovanadium is usually produced via reduction in an electric furnace in the presence of iron or iron ore. The obtained ferrovanadium can be used without further refinement. The pig iron containing vanadium can be oxygen lanced to produce a slag containing 12–24% vanadium. This can be further smelted at high temperature or chilled and processed using solvent extraction to produce vanadium pentoxide (Moskalyk and Alfantazi, 2003).

The main global supplier of vanadium is China, which had a market share of 53% in 2017 (EC, 2017b). South Africa and Russia follow, with a market share of 25% and 20%, respectively. With worldwide reserves totalling over 13.5 million tonnes (about 10 million in China and Russia, and 3.5 million in South Africa), it was estimated that demand can be met for at least another century at the present rate of consumption (EC, 2011). There is no extraction of vanadium in Europe. This is either to limited knowledge of the availability of vanadium in the European Union, or to economic and societal factors that negatively affect exploration (EC, 2017b). Despite China being the global supplier, the main share of European sourcing (60%) comes from Russia.

In China, mining is done in the Sichuan and Anhui provinces. In addition, vanadium-containing slags are imported from New Zealand, Russia and South Africa (Moskalyk and Alfantazi, 2003). Chengde Xinghua Vanadium Chemical Co. Ltd., Emei Ferro-Alloy Co. Ltd., Hengyang Manganese Product Works, Jinhzhou Ferro-Alloy Co. Ltd., Nanjing Ferro-Alloy Works, Panzhihua Iron and Steel Group, and Shanghai Non-Ferrous Metals Research Institute produce a wide range of vanadium products, including metal, pentoxide and ferrovanadium. In South Africa, in the beginning of the century, four companies were operational: Highveld Steel and Vanadium Corporation, Vametco Minerals Corp., Vanadium Technologies (Vantech), and Rhombus Vanadium Holdings Ltd. (Rhovan). The first in the list was the largest and operated two plants, the Vantra (production of vanadium pentoxide from ore and slag) and Wapadskloof facilities (production of vanadium trioxide and others). In Russia, deposits of vanadium are located in the Ural Mountains (Katschkanor and Sverlov regions), Siberia, and some areas in the far east, and northwest. The vast majority of the pentoxide is produced from slag by Nizhny Tagil Iron & Steel Works. Pentoxide and ferrovanadium are also produced by Kachkanar Vanadium Mine and Concentrator, Chusovskoy Iron and Steel Works, and JSC Vanadly-Tula.

![Fig. 8. Typical processing routes to produce vanadium pentoxide and vanadium metal.](Image)
6. Recycling

Data on recycling rates of vanadium vary widely. In 2014 the EU Commission estimated that vanadium is not recycled at all (EC, 2014b). Only recently, for the EU an end of life recycling input rate of 44% was reported (EC, 2017b; Eurostat, 2018). For the USA, according to the U.S. Geological Survey about 40% of vanadium is recycled from chemical process catalysts (Polyak, 2019), petroleum residues, utility ash, and vanadium-bearing pig iron slag.

The amount of spent desulfurization catalysts grows rapidly due to the increasing demand of related markets, and a limitation of the regeneration. The reasons for significant increase in the waste production can be summarized as follows: (1) a substantial expansion in the capacity of distillate hydrotreating to sustain a sulfur with extra-low level, (2) decreased operation times as the consequence of harsh operation environment and source having high content of sulfur, and (3) prompt deactivation together with deficiency of reactivation process (Kim et al., 2018). Currently, the market for fresh hydro-processing catalysts approaches 120,000 tons per year (Kim et al., 2018). Composition of the catalyst waste differ. Erust et al. determined composition with approximately 6% V2O5, 2% Al2O3, 1% Fe2O3 and 60% SiO2; and the rest ly other waste components.

The slag is usually composed of oxides such as: CaO, Fe2O3, SiO2 and MgO, with smaller amount of Al2O3, MnO, P2O5 and TiO2. The vanadium ends up in a BOF slag containing approximately 5% of vanadium pentoxide (V2O5) (Waligora et al., 2010). The U.S. Geological Survey also reports that only some tool steel scrap was recycled primarily for its vanadium content. It is further outlined by the U.S. Geological Survey that this only accounted for a small percentage of total vanadium used (Polyak, 2018).

Another secondary source of vanadium is the oil fly ash produced by the combustion of crude oil (Navarro et al., 2007). Depending on the chemical composition and process, fly ash can contain from 2 to 50% of vanadium.

Both, vanadium and niobium are primarily used as an alloying element for different steel grades. About 90% of vanadium (EC, 2014b) and niobium (TIC, 2016) go into steel alloys. It is thus evident that for both elements end-of-life steel grades containing vanadium and/ or niobium are potential sources for recycling. It has been reported that in practice niobium is not recycled as pure metal but a niobium bearing alloy is re-melted into a similar alloy (Cunningham, 2004). It has further been outlined that due to the low content of niobium in steel (<1%) niobium bearing steels are not collected separately and during recycling of steel niobium is diluted. This is a so called non-functional recycling in which niobium is lost (Tkaczyk et al., 2018). As a matter of fact the recycling rate of niobium is de facto zero (EC, 2017b). The situation of vanadium is quite similar. Even if concentration of vanadium in steel (1%) is diluted the future vanadium containing batteries must be considered as a source for vanadium recycling.

Stone coal is considered to be an alternative source of vanadium. However, due to the low vanadium grade, complex chemical composition and various occurrences of vanadium of stone coal, vanadium recovery from stone coal is usually confronted with the problems of enormous ore handling quantity, significant acid consumption and notable production cost (Liu et al., 2017). Currently vanadium recycling results into the production of V2O5 from V-bearing raw materials including secondary materials are reviewed in a general flowsheet in Fig. 9 displaying the hydrometallurgical route.

6.1. Roasting and leaching of vanadium from the secondary sources

Vanadium is recovered as sodium vanadate after roasting the slag in a multi-hearth furnace or rotary kiln with addition of sodium carbonate or sodium sulphate/chloride. In some cases, more additives such as lime are added into the process (Xiao et al., 2010). However, the salt roasting is a traditional route for production of soluble vanadium substances, it is time-demanding process, which requires high temperature (800–900 °C) conditions and it is related to the formation of hydrogen chloride or elemental chlorine (Li and Xie, 2012). The mechanism of the roasting is according to the reactions below. They represent roasting conditions using the oxygen (reaction (6.1.1)) and with the presence of water (reaction (6.1.2)). Either oxygen or water are required to drive the reaction towards the formation of sodium metavanadate.

\[
\begin{align*}
\text{V}_2\text{O}_5 + 2\text{NaCl} + 1/2\text{O}_2 & \rightarrow 2\text{NaVO}_3 + \text{Cl}_2 \quad \text{(without vapor)} \\
\text{V}_2\text{O}_5 + 2\text{NaCl} + \text{H}_2\text{O(g)} & \rightarrow 2\text{NaVO}_3 + 2\text{HCl} \quad \text{(with vapor)}
\end{align*}
\]

In general sodium salts roasting process generates harmful gases, such as Cl2, SO2 or HCl. Those by-products can cause the corrosion of the equipment and same way can negatively affect the environment if not treated properly. The efficiency of the roasting is around 80%, thus, several roasting steps are required to achieve sufficient extraction.

The calcification roasting is considered to be a cleaner alternative to the roasting using sodium carbonate. In the calcination roasting the vanadium slag is processed with limestone or lime. Vanadium is transformed from the vanadium-bearing spinels into calcium vanadates. Vanadium in the vanadium slag is present as FeV2O4 spinels which are enrapured by the olive phase Fe2SiO3 (Zhang et al., 2012). After the roasting, the olive phase Fe2SiO3 is diluted. This is a so called non-functional recycling in which niobium is lost (Tkaczyk et al., 2018). As a matter of fact the recycling rate of niobium is de facto zero (EC, 2017b). The situation of vanadium is quite similar. Even if concentration of vanadium in steel (1%) is diluted the future vanadium containing batteries must be considered as a source for vanadium recycling.

Innovative NaOH-added pellet was applied to replace traditional Na2CO3-Na2SO4-NaCl-added pellet (Ji et al., 2017). Vanadium extraction was increased from traditional 80% at 800 °C to current 99% at 700 °C.
Vanadium recovery from the sources starts directly with the leaching or alkaline roasting followed by the leaching. Valency state of vanadium in the solution can be +2, +3, +4 and +5. If the leaching is performed in the presence of the oxygen or in the presence of the oxidative agent, vanadium oxidizes to a stable form of pentavalent vanadium. Controlling parameters for vanadium valent state are vanadium molarity in the solution, pH of the solution, and potential (Eh) of the solution. In the acid region the predominant specie of vanadium is VO₂⁺. In the alkaline region at pH above 13, VO₄³⁻ is the predominant specie (Gupta and Krishnamurthy, 1992). Ability to control vanadium valent state via pH is utilized in the leaching process. Secondary source of vanadium – slag is processed via acidic leaching using mostly mineral acids. Acidic leaching is then followed by the neutralization with alkaline media. Using acid, the vanadium in the slag can be recovered as VO₄³⁻ or VO₂⁺ ions. In the neutralization step, the VO₄³⁻ and VO₂⁺ ions can be converted to sodium vanadate. In general, leaching of vanadium is performed using sulfuric acid (and oxidation/reduction agent) can be expressed by following chemical reactions of vanadium oxides:

\[
\begin{align*}
V_2O_5 + H_2SO_4 & \rightarrow (VO_2)_2SO_4 + H_2O \\
V_2O_3 + 2H_2SO_4 + H_2O_2 & \rightarrow 2VOSO_4 + 3H_2O \\
3VO_2 + 3H_2SO_4 & \rightarrow 3VOSO_4 + 3H_2O
\end{align*}
\]

Novel approach to improve leaching with the sulfuric acid was developed using microwave heating (Tian et al., 2019) as the alternative to the electric heating. Leaching efficiency of vanadium was improved by 50%. The electro-oxidation is another alternative method for the improvement of the leaching efficiency due to the oxidation of vanadium (Liu et al., 2016).

Alkaline leaching with and without the oxidation has been performed to recover vanadium from the secondary sources. Several oxidative agents were used for the leaching to recover vanadium, and chromium. Yang et al. (2010) applied NaOH and H₂O₂. Air was applied as the oxidative agent for the leaching with NaOH (Guo et al., 2015), and oxidizing roasting followed by leaching with NaOH (Yang et al., 2014a) was also tested. The vanadium leaching efficiency in each process was in the range of 75–90%. Selective oxidation of V⁴⁺ to V⁵⁺ was performed using manganese dioxide (Chen et al., 2017). Alkaline leaching using NaOH was also applied for vanadium recovery from spent catalysts (Kim et al., 2015).

The research focused the recovery of vanadium from the primary and secondary sources is significantly extensive. There are several works applying roasting or direct leaching summarized in the Table 12.

A novel acid leaching method for direct recovery of vanadium from Linz-Donawitz converter slag avoiding pyrometallurgical roasting process is suggested by Mirazimi et al. (2015). At the same time, a direct leaching of vanadium-containing magnetite by mixture of nitric and sulfuric acids is suggested by Nejad et al. (2018) as an optimized approach without pyrometallurgical step. Vanadium can be recovered from the solution by precipitation using from using ammonium salts (Biswas et al., 1985; Liu and Sui, 2002; Wen et al., 2019; Ye et al., 2012; Zeng and Yong Cheng, 2009). In general, the precipitation efficiency depends mostly on the concentration of ammonium salt and very often 100% recovery rate is achieved. Use of ammonium chloride is preferred due to economic reasons. However, it is necessary to achieve requested efficiency, ammonium chloride has to be applied in excess, since it desalinizes the ammonium vanadate (V) due to the occurrence of the common ion effect (Mazurek, 2013). Satisfactory efficiency can be achieved by precipitating vanadium using barium hydroxide, since the Ba₃(VO₄)₂ is weakly soluble in aqueous solutions (Zeng and Yong Cheng, 2009). Short kinetics and use of stoichiometric amounts of Ba(OH)₂ can lead to the efficiency of 90% for vanadium recovery.
Despite the advantage vanadium recovery from the secondary source, such approach leads to the generation of the secondary products. For example, approximately 30–50 tons of ammonia waste water based on Na₂SO₄, (NH₄)₂SO₄ and/or NH₄Cl per ton of V₂O₅ product is generated (Li et al., 2017b) after the precipitation and recovery of the vanadium.

Common methods to recover and purify vanadium from the solution is solvent extraction or ion exchange.

### 6.2. Recovery of vanadium using solvent extraction

For vanadium recovery by solvent extraction several extractants were used. Among these D2EHPA (Di(2-ethylhexyl)phosphoric acid) was used in plat operations. D2EHPA extracts V⁴⁺ more strongly than V²⁺ and extraction coefficients of V⁴⁺ are high enough to be useful in a practical process. The pH-extraction isotherms exhibit that the extraction order would be Fe³⁺ > V⁴⁺ > VO₂⁺ > Ca²⁺ > Mg²⁺ > Fe²⁺ > K⁺, Na⁺ (Li et al., 2011). It follows from there that at given conditions, D2EHPA will extract Fe³⁺ together with vanadium but not Fe²⁺. In order to selectively recover vanadium and to avoid the extraction of iron, it is needful to reduce trivalent iron to divalent. Mechanism of D2EHPA reaction with metal ions is as following (Li et al., 2012, 2011):

\[
\text{VO}^{2+} + 2\text{H}_2\text{A}_{2(0)} \rightleftharpoons \text{VOA}_2\cdot2\text{HA}_{(0)} + 2\text{H}^+ \quad (6.2.1)
\]

\[
\text{Fe}^{3+} + 3\text{H}_2\text{A}_{2(0)} \rightleftharpoons \text{FeA}_3\cdot3\text{HA}_{(0)} + 3\text{H}^+ \quad (6.2.2)
\]

\[
\text{Fe}^{2+} + 2\text{H}_2\text{A}_{2(0)} \rightleftharpoons \text{FeA}_2\cdot2\text{HA}_{(0)} + 2\text{H}^+ \quad (6.2.3)
\]

In the industrial processing the concentration of DEHPA is sustained from 0.2 to 0.4 M and the operational pH is 2. Also, Na₂S or NaHS is used as the reduction agent. This treatment reduces pentavalent vanadium. For the recovery of the vanadium to the aqueous phase, dilute sulfuric acid is used (Gupta and Krishnamurthy, 1992). The SOTEX process which recovered vanadium and nickel from ash and soot residues has been developed by MEAB. The dominating metal constituents of the residues are vanadium, nickel and iron, together with high concentration of magnesium. The leaching with sulfuric acid yielded to about 55% of V⁴⁺ and for Ni²⁺ it was 95%. A final (post) leach with sodium hydroxide dissolved remainders was still applied in many processes of vanadium recovery (Li et al., 2010). A final test with sodium hydroxide dissolved remainders was still applied in many processes of vanadium recovery (Li et al., 2010).
et al., 2013a; Li et al., 2011; Zeng and Yong Cheng, 2009). Addition of TBP to the organic phase reduces the unfavourable effects of M2EHPA (mono (2-ethylhexyl)phosphoric acid) which is present in commercial D2EHPA and moreover, it is an effective phase modifier since it improves separation efficiency and phase separation (Cheraghi et al., 2015). It was reported that D2EHPA extracts Fe$^{3+}$ but not Fe$^{2+}$ and V$^{4+}$ is extracted more strongly than V$^{5+}$. Sodium sulphide, sodium hydrosulphide or sodium sulphate can be used as reduction agents to reduce Fe$^{3+}$ to Fe$^{2+}$ and V$^{5+}$ to V$^{4+}$. Extraction is usually carried on at pH around 1–2. Vanadium stripping can be done using sulfuric acid. D2EHPA can be used for recovery of Mn and Mg by increasing pH at 3–4.

One of the developments in the field of solvent extraction is the introduction of some new organophosphines and their sulfur analogues as extractants as Cyanex 272 and Cyanex 301. Cyanex 272 can extract V$^{5+}$ and the comparison study (Li et al., 2012) showed that D2EHPA is a stronger extractant than Cyanex 272. Cyanex 272 also extracts Fe$^{3+}$ and there is a lack of the information about extraction characteristic related to V$^{4+}$. On the other hand, Cyanex 301 can extract V$^{5+}$ and vanadium can be separated from Fe$^{3+}$ at pH 1. Cyanex 923 was successively applied for V$^{5+}$ recovery at pH 1. Extractant LIX 63 was used for V$^{5+}$ (Zhang et al., 1996) and V$^{5+}$ (Zeng and Cheng, 2010) at pH around 1 was used and excellent separation from Fe$^{3+}$ has been reported. Even good separation from Al$^{3+}$ was mentioned. Cyanex 272 (0.6 M) was also applied for the separation of Ni$^{2+}$ and V$^{4+}$ recovered from the fly ash (Noori et al., 2014). Addition of TBP as a modifier raised separation factor of V over Ni(SF$_2$)–440. McCabe–Thiele diagrams showed that two extraction stages are needed for the separation. Solvating extractant Cyanex 923 was applied to separate V$^{5+}$ from Fe$^{3+}$ (Tawkoli and Dreisinger, 2014). Cyanex 923 showed the best selectivity for V$^{5+}$ over Fe$^{3+}$ by extracting of VO$_2$SO$_4$ in the system.

Amines have been also used in vanadium recovery (Wen et al., 2017). The advantage of amines is that it has two active N atoms and one active N atom, and can extract vanadium selectively (Jing et al., 2017; Ning et al., 2014). Only pentavalent vanadium forms anionic complexes. It the tetravalent state, vanadium is not extracted by amines. Among the various amines, the tertiary and quaternary amines have found maximum use and have been applied in praxis. Alamine 336 and Alamine 308 was tested for vanadium recovery after leaching of the spent catalysts (Kim et al., 2018). It was determined that optimal pH was 2.5. It was concluded that Alamine 308 performed better than Alamine 336, since over 2000 mg/L of vanadium was recovered. Research dealing with the extraction of vanadium and impurities via solvent extraction are summarized in Table 13.

Comparison of ion exchange and solvent extraction for vanadium recovery from sulfuric acid leach solutions of stone coal was published in a work (Li et al., 2013a). Leaching of roasted stone coal with sulfuric acid resulted in a mixed vanadium solution containing Fe$^{3+}$, Fe$^{2+}$, Al$^{3+}$ and Mg$^{2+}$. An anion exchange resin ZGA414 was tested as its optimum adsorption capacity compared with D202, D453, D301FC and ZGA351 resins, and D2EHPA and TBP diluted with kerosene were employed in solvent extraction. Ion exchange tests indicated that only V$^{5+}$ was loaded from the synthetic solution at pH > 1.5, while it was difficult to separate V$^{5+}$ from Fe$^{3+}$. Solvent extraction experiments revealed that V$^{5+}$ had a better extraction ratio than that of V$^{4+}$, while Fe$^{3+}$ had a serious effect on the extraction of V$^{5+}$. The co-extraction ratio of Al$^{3+}$ and Mg$^{2+}$ can be decreased by controlling their concentrations lower than 10 g/L. Counter-current experiments with D2EHPA presented that 99% of V$^{5+}$ was extracted from the real leach solution after reduction process, leaving most of Fe$^{3+}$, Al$^{3+}$ and Mg$^{2+}$ in the raffinate. Both solvent extraction and ion exchange can be applied in vanadium recovery. D2EHPA has been already applied for vanadium recovery in the industrial applications and seems to be promising extractant since it allows to extract V$^{4+}$ and V$^{5+}$. However, D2EHPA extracts Fe$^{3+}$ and it can cause the difficulties in vanadium recovery and use of reduction agent would be required. LIX 63 seems to be also suitable extractants since it extracts V$^{4+}$ and V$^{5+}$ over the iron.

6.3. Recovery of vanadium using ion exchange

Ion exchange has been also applied for vanadium recovery. A strong anion exchange resin such as Amberlite IRA-400 has been used in uranium ore process. It may be added that the resin extracts along with the vanadium the major impurity - iron. This is, however selectively removed from the loaded resin with NH$_4$Cl and HCl prior to the elution of vanadium. Ion exchange is mostly used in the processes of spent hydrodesulfurization catalysts to recover molybdenum and vanadium (Chen et al., 2003; Li et al., 2009). To recover V$^{5+}$ from the sulfuriic media strong anion exchange resin DOWEX 21 K (Zippirian and Raghavan, 1985), weak anion exchange resin D314 (Li et al., 2009; Zeng et al., 2010) and strong cation exchange resin DOWEX 50-W, have been used for vanadium recovery. The possibility of vanadium (V$^{4+}$, V$^{5+}$) separation from other metals was performed using DOWEX50-X8 (Fritz and Abbink, 1962). Vanadium was separated from Mn$^{2+}$ which was not absorbed. Subsequently V$^{5+}$ was separated from Ti$^{4+}$ and Fe$^{3+}$ with HCIO$_4$. Seeing that leaching solution contains also other metals, it should be mentioned that heavy metals can be selectively removed from acid leach solutions using DOWEX™ M4195 resin. Metal removal from very strong acids may be effective using strong base anion exchange resin such as DOWEX 21 K resin. Ion exchange has been applied for recovery of vanadium from several primary and secondary sources. Ion exchange has been applied for vanadium recovery from the stone coal (Li et al., 2013c; Zeng et al., 2009), from the waste generated in the Bayer process (Zha et al., 2010), from the wastewater (Keränen et al., 2015), spent catalysts (Nguyen and Lee, 2013), and steel making slags (Gomes et al., 2017). Recovery from the alkaline media using D403 has been reported in (Zhu et al., 2017). Several other works applying ion exchange for vanadium separation and recovery are summarized in the Table 14.

6.4. Pyrometallurgical processing of vanadium-containing sources

Pure vanadium can be produced from vanadium pentoxide via a metallothermic reaction with calcium or aluminum. Ferrovandium is produced via the aluminothermic reduction of vanadium sludge (Suri et al., 1983):

\[
\text{nFeO} \cdot \text{V}_2\text{O}_5 + (2*(5 + n))/3 \text{Al} \rightarrow (\text{nFe}) \cdot (2 \text{V}) + ((5 + n)/3)\text{Al}_2\text{O}_3
\]

(6.4.1)

\[
\text{nCaO} \cdot \text{V}_2\text{O}_5 + 4\text{Al} + 1/3\text{Fe}_2\text{O}_3 \rightarrow 2(\text{Fe}) \cdot (2 \text{V}) + 2\text{Al}_2\text{O}_3 + \text{nCaO}
\]

(6.4.2)

Vanadium electro-aluminothermic processing is characterised by materials losses when vanadium droplets and vanadium oxides are mixed with the slag (see Table 15).

A designated system model was prepared (Lundkvist et al., 2013) by simulating the implementation of a two-step BOF blowing procedure and a slag reduction process in an integrated steel production system. The aim was to analyse the system effects from extracting vanadium as an FeV alloy and improve the slag recycling and total material efficiency in the system. Smelting reduction was applied for the recovery of vanadium and chromium from an LD slag. An in-plant by-product melting process (IBPM) was tested using steel slags, fine-grained wastes, such as EAF dust, millscale, oily millscale, BOF dust, BF dust, hydroxide sludge and scrap resi-
Some of the studies dealing with recovery of vanadium from different leaching media using ion exchange.

| System tested | Remarks | Metals | pH | Reference |
|---------------|---------|--------|----|-----------|
| D2EHPA | Calculated standard molar enthalpy of the reaction indicated the endothermicity of extraction reaction between VO2+ and D2EHPA. | V(IV) | – | Razavi et al., 2018 |
| Primary amine | Three extraction complexes generated in organic phase, and the stoichiometric ratios were 4/3, 2 and 3 for the extraction complexes (RNH2)4/H2O, (RNH2)2/H2O and (RNH2)2/H2O. | V(IV) | – | Wen et al., 2019 |
| D2EHPA + PC88A | For three extract systems, the extraction ability of vanadium follows the order D2EHPA + PC88A > D2EHPA > PC88A, while the selectivity for primary metal ion (Fe and Al) follows the order D2EHPA + PC88A > PC88A > D2EHPA. | V(IV), V(III), Fe(III), Al(III) | 2 | Shi et al., 2017a |
| D2EHPA + EHEHPA | The mixture system in the presence of complexing agents exhibit a higher extraction efficiency and require a lower acid consumption during the stripping process of vanadium. | V(IV) | 1.6 | Zhang et al., 2016a |
| D2EHPA + TBP | TBP has no synergetic effect on the VO2+ extraction except in the experiments conducted at 60°C. | V(IV) | 1.8 | Cheraghli et al., 2015 |
| D2EHPA (from HCl) | V(IV) can be separated from other metal ions such as Mg2+, Ni2+, Zn2+, Ca2+, Al3+ and Cu2+ in HCl solution. | V(IV), Fe(III) | 1 | Hu et al., 2014 |
| Mextral 973H | The extraction of V(IV) is strongly dependent on solution pH and the separation efficiency (E[0 V/F]) between V(IV) and Fe(III) can be greater than 720 when the solution pH < 0.5. | V(IV), Fe(III) | 0.5 | Zhang et al., 2018b |
| Triallylamine-N235 + TBP | Vanadium was successfully extracted by a three-stage counter-current process using 20% N235 and 5% tri-ethyl phosphate at an organic-to-aqueous (A/O) phase ratio of 2.1. | Fe, Al, Mg, K, Ca, P, Si, V(V), Fe(III), U(VI), Sb(V), and Al(III) | 2.0 | Yang et al., 2016 |
| Z-ethyl-1-hexanol | 2-ethyl-1-hexanol is found to be a selective extractant for the separation of V(V) over Fe(III), Cu(II), Sb(III) and Al(III). | | | Razavi et al., 2017 |
| Alamine 336 + TBP | The extraction isotherm, constructed through McCabe–Thiele plot, predicted two stages counter current process where about 99% vanadium can be extracted. | Mo, V | 1.25 | Kim et al., 2015 |
| Alamine 336 + octanol | Vanadium can be more easily extracted over tungsten from ammonium tungstate solutions, dropping vanadium to 0.004 g/L with tungsten loss below 5% after six-stage counter current extraction. | W, V | 8.7 | Wang et al., 2018 |
| 10% D2EHPA, 5% TBP and 85% sulphonated-kerosene system | It was necessary to make ferrocene ion reduced into ferrous ion before extracting vanadium. Sodium sulfite was used as the reductant. The reduction rate of ferrocene ion could reach 98.2%. | V(IV), V(III), Fe(III) | – | Deng et al., 2010 |
| D2EHPA, EHEHPA, Cyanex 272 | D2EHPA was found to be a stronger extractant, having greater pH functionality than EHEHPA and Cyanex 272. The species were found to be VOR2(HR)2 in the high acidity and VOR2 in low acidity. | V(IV) | – | Li et al., 2012 |
| Cyanex 272, PC88A, TR-83 | V can be selectively extracted over Al with TR-83 and PC-88A. Complete selective stripping of V from Cyanex 272 excluding Fe can be done using aqueous ammonia solution. | V(IV), Mo(IV), Al(III), Fe(III) | 1.51 | Zeng and Yong Cheng, 2009 |
| Cyanex 301 | By using Cyanex 301 as extractant, V(IV) can be separated from Cu(II) and Zn(II) (after few stages). | V(IV), Cu(II) | >1 | Karmakar and Bisisio, 2019 |
| Cyanex 923 | The species extracted into the organic phase was VO4H2O with one molecule of Cyanex 923. | V(IV) | 1–2 | Wang et al., 2009 |
| LIX 63 | Complete recovery of Mo(IV) and V(IV) from Al3+, Fe3+, Co3+ and Ni2+ can be achieved at pH 1.2–1.5. | Mo(IV), V(IV), Al(III), Fe(III), Co3+, Ni2+, V(IV), Fe(III), 1.2–1.5 | 1.5 | Zeng and Cheng, 2010 |
| LIX 63 | The separation factor excellent separation of V(IV) from Fe(III). | Mo(IV), V(IV), Al(III), Fe(III), Co3+, Ni2+, V(IV), Fe(III), 1.2–1.5 | 1.5 | Zeng and Cheng, 2010 |
| Primene 81R, Alamine 336 | The extracted species for vanadium at pH 4.5 is (H2O)4V10O28(HR)2 with x = 0, 1, 2, and at pH 8 are several vanadates: (VO4)2O2–, (VO4)2O– and (VO4)3+ . | V(IV) | 8 | Lozano et al., 2003 |

Some of the studies dealing with recovery of vanadium from different leaching media using ion exchange.

| Exchanger | Remarks | Metals | pH | Reference |
|-----------|---------|--------|----|-----------|
| DOWEX 21 K | V loading is possible in oxidizing atmospheres since the predominant vanadium species in solution is the anionic complex VO2(OH)2. | V(IV) | 4 | Zipperian and Raghavan, 1985 |
| DOWEX 50-W | EDTA was used to form stable iron (III) EDTA complexes to remove iron from the resin and to increase final purity of vanadium. | V(IV), Fe(III) | – | Gupta and Krishnamurthy, 1992 |
| D314 | Loading of vanadium on the resin can reached 280 mg/mL with overall recovery 98.6% V was absorbed in the forms of VO4 and HV2; the maximum distribution ratio of V with the resin was 1475 at pH 4.3 and 35 °C. | V(IV) | 3.2 | Zeng et al., 2009 |
| DDAS, CUW, CW-2 (D2EHPA)-impregnated Amberlite 200 resin | More than 99.5% V and<0.27% Mo was extracted with a contact time of 60 min. One single column, consisting of non-modified Amberlite 200 resins in the top section and D2EHPA-impregnated Amberlite 200 resins in the lower section, can be used to separate Ni, V and Mo ions. | V(IV), Mo(IV) | 7.4 | Li et al., 2009 |
| Dowex50W-X8 | V was separated from Co2+, Mn2+, Ni2+, Zn2+ and other metals. | V(IV), V(III), Co2+, Fe3+, Mn2+, Ni2+, Ti4+, Zn2+ | – | Fritz and Abbink, 1962 |

Due (Ye et al., 2003). Iron, vanadium, chromium and nickel were recovered in a metal (alloy) phase after applying the IBPM. A German company, GfE Metalle und Materialien GMBH, developed a combination of pyrometallurgical and hydrometallurgical processes, where a pyrometallurgical approach is used for obtaining cast vanadium concentrate for the further extraction of pure vanadium (Marafi et al., 2010).

Microwave-assisted pyrometallurgical processes for the calcination (Salakjani, Nikolski, and Singh, 2017) of ores are emerging applications for vanadium-containing ore processing. Specifically,
when applied to a vanadium slag, it facilitates materials conversion at lower temperature (Gilligan and Nikoloski 2020).

7. The study of technological innovation change

The rich literature about the vanadium recovery proves the strong interest for this topic, showing innovative experimental approaches for the exploitation of several kinds of waste. Nevertheless, many treatments need specific reaction conditions that make the scale-up difficult. In order to have an overview of the options designed for a real implementation, a deepened study of published patents and the European projects was carried out, following the approach used by Amato and Beolchini (2018). The study of technological innovation change allows the identification of innovative markets, promising from an economic point of view (Amato and Beolchini, 2018; Garcia and Calantone, 2002; Rocchetti et al., 2018).

As concern the patents, the free access Espacenet platform was chosen as research tool (http://worldwide.espacenet.com), since it ensures the overview of the worldwide inventions. The “vanadium recycling” was used as keyword for the patent researches and an interval around 50 years (between 1954 and 2018) was taken into

| Project title                                                                 | Year       | Coordinating country | Kind of waste                 |
|------------------------------------------------------------------------------|------------|----------------------|-------------------------------|
| The recovery and recycling of vanadium and nickel products from the combustion residues of Orimulsion and other fuels | 1992–1995  | United Kingdom       | Fly ash                       |
| Optimization of selective chlorination of spent hydro-desulfurization catalysts | 1991–1993  | Spain                | Spent catalysts              |
| ERA-MIN                                                                       | 2011–2015  | France               | Steel slags                  |
| Reclaiming of metals contained in spent catalysts used in petroleum refining petrochemistry and chemistry | 1992–1995  | France               | Spent catalysts              |
| The in-plant by-product melting (IPBM) process                                | 1996–1998  | Sweden               | Steel slags                  |
| New system for recovery of valuable metals from exhausted catalyst            | 1997–1998  | Italy                | Spent catalysts              |
| Recovery of valuable metals from the TiO₂ production process                | 1983–1985  | United Kingdom       | TiO₂ production process waste |
| Vanadium and associated materials beneficiation out of residues and complex ores | 1983–1985  | Italy                | Various residues             |
| Valuable metal recovery from residues: Mo, Co and Ni from spent catalysts     | 1988–1990  | Spain                | Spent catalysts              |
| Patent number | Patent title                                                                 | Year | Reference                        |
|---------------|------------------------------------------------------------------------------|------|----------------------------------|
| US2018297856  | Vanadium recovery method                                                     | 2018 | Jung Myungwon, 2018             |
| US2018280941  | Method for recycling denitrification catalyst (Monsanto Chemicals, 1964; Robinson and Bentley, 2002) | 2018 | Kiyonaga et al., 2018            |
| CN108160310   | Comprehensive recycling method for vanadium-contaminated coal-pyrite         | 2018 | Du et al., 2018                  |
| CN108165741   | Method for leaching metal in vanadium titan-magnetite through full acid method | 2018 | Li et al., 2018                  |
| CN108149015   | Method for extraction of valuable components in vanadium-titanium magnetite through oxygen-rich selective leaching | 2018 | Zhang et al., 2018a              |
| CN108126828   | Beneficiation method of black shale type vanadium ore vanadium enriched discarding-tailing | 2018 | Deng et al., 2018                |
| CN108048668   | Method for recycling chromium and vanadium from chromium and vanadium containing slag | 2018 | Xue et al., 2018                 |
| CN108018437   | Low-temperature comprehensive recycling technology for iron, vanadium and titanium of vanadium-titanium magnetite | 2018 | Zhang, 2018                      |
| CN107970910   | Method for recycling waste vanadium catalyst                                | 2018 | Xie et al., 2018                 |
| CN107904403   | Method for comprehensively recycling vanadium-titanium series denitrification spent catalyst | 2018 | Gao et al., 2018                 |
| CN107892317   | Method for recovering vanadium from calcined vanadium precipitation tailings and preparing nano calcium carbonate | 2018 | Zhao et al., 2016a               |
| CN10794326    | Recycling method used for vanadium-containing magnetic substances             | 2018 | He et al., 2018                  |
| CN107758940   | Recycling treatment method for laboratory vanadium-containing waste liquid    | 2018 | Zhao et al., 2018b               |
| CN107739832   | Recovery method for vanadium in oxygen-enriched air roasting acid vanadium precipitation waste liquid | 2018 | Li et al., 2018                  |
| CN107699095   | Method for recycling tungsten and vanadium from waste SCR denitration catalyst | 2018 | Xi et al., 2018                  |
| CN107620090   | Recycling method of vanadium and manganese in wastewater with deposited vanadium | 2018 | Chen et al., 2018a              |
| TW201821621   | Method for recycling metal composition from discarded denitification catalyst | 2018 | Chen et al., 2018b              |
| CN107572586   | Method for recycling V<sup>2+</sup>O<sup>5-</sup> from acid manufacturing spent vanadium catalysts | 2018 | Zhou et al., 2018               |
| CN107557599   | Method for recycling tungsten and vanadium from waste SCR denitration catalyst | 2018 | Zhang et al., 2018c             |
| CN107500352   | Method for producing high-purity ammonium vanadate through low-temperature precipitation | 2017 | Song et al., 2017a              |
| CN206721309   | Method for recycling vanadium from waste SCR catalyst and treatment method thereof | 2017 | Wang et al., 2017               |
| CN107416902   | Method of recycling component substances of waste SCR denitration catalyst at low cost | 2017 | Wang, 2017b                     |
| CN107416904   | Method of recycling component substances in a waste SCR denitration catalyst | 2017 | Wang, 2017b                     |
| CN107312936   | Method for recycling vanadium element from Panshihua City vanadium titan-magnetite blast furnace slag | 2017 | Dai et al., 2017                |
| CN107287493   | Vanadium-contained waste recycling utilization method                        | 2017 | Li et al., 2017c                |
| CN107254587   | Method for decomposing vanadium-containing steel slag through sodium bicarbonate for recycling vanadium | 2017 | Li et al., 2017d                |
| CN107090551   | Direct vanadium extracting method for vanadium-titanium magnetite             | 2017 | Du et al., 2017                 |
| CN107058764   | Method for recycling vanadium from corundum slag                            | 2017 | Guo et al., 2017                |
| CN100957962   | Method and system for treating vanadium extraction tailings                  | 2017 | Song et al., 2017b              |
| CN100957963   | System and method for testing vanadium extraction tailings                    | 2017 | Song et al., 2017c              |
| CN100947864   | System for recovering heavy metal from waste SCR catalysts and treatment method thereof | 2017 | Song et al., 2017c              |
| CN107012276   | Comprehensive utilization method for vanadium-titanium magnetite             | 2017 | Deng et al., 2017               |
| CN107012331   | Method for recycling vanadium from waste containing molybdenum and vanadium and method for preparing vanadium pentoxide | 2017 | Yang et al., 2017             |
| CN106995879   | Low-grade chromium-contained type vanadium-titanium magnetite sodium treatment oxidation-leaching extracting method | 2017 | Xue et al., 2017               |
| CN106978544   | System and method for treating vanadium and chromium slag of rotary furnace  | 2017 | Song et al., 2017d              |
| CN106978543   | System and method for treating vanadium and chromium slag of rotary furnace  | 2017 | Song et al., 2017h              |
| CN106978542   | System and method for processing vanadium and chromium slag of converter      | 2017 | Song et al., 2017f              |
| CN106967885   | Vanadium extraction tailing treatment method and system                       | 2017 | Song et al., 2017g              |
| CN106893877   | Method for extracting vanadium and chromium from vanadium chrome mixed solution | 2017 | Wang et al., 2017c              |
| CN106884090   | Sub-molten salt method for totally recycling vanadium, tungsten and titanium from waste denitration catalyst | 2017 | Wang et al., 2017c              |
| CN106868311   | System and method for handling revolving furnace vanadium-chromium slag      | 2017 | Song et al., 2017h              |
| CN106808312   | System and method for handling revolving furnace vanadium-chromium slag      | 2017 | Song et al., 2017i              |
| CN106793939   | Method for repairing vanadium polluted soil and recovering vanadium and treatment equipment | 2017 | Zhang and Cao, 2017           |
| CN106755668   | Blast furnace smelting method for vanadium-titanium magnetite                | 2017 | Bai, 2017a                     |
| CN106756119   | Method and system for removing phosphorus and extracting vanadium from high-calcium and high-phosphorus vanadium slag | 2017 | Song et al., 2017j              |
| CN106756120   | Method and system for processing high-calcium and high-phosphorus vanadium slag | 2017 | Song et al., 2017k              |
| CN106756070   | Method and system for processing high-calcium and high-phosphorus vanadium slag | 2017 | Song et al., 2017l              |
| CN106756121   | Method and system for removing phosphorus and extracting vanadium from high-calcium and high-phosphorus vanadium slag | 2017 | Song et al., 2017m              |
| CN106636646   | Method for efficiently extracting vanadium and tungsten from waste SCR denitration catalyst | 2017 | Xia et al., 2017               |
| CN106636628   | Treatment system and method for vanadium extraction tailings                 | 2017 | Song et al., 2017n              |
| CN106636560   | Blast furnace smelting method of vanadium-tin-magnetite                      | 2017 | Bai, 2017b                     |
| CN106498165   | Method for recovering nickel and vanadium from waste FCC (Fluid Catalytic Cracking) catalyst through molten chlorination volatilizing | 2017 | Wang et al., 2017b             |
| CN106521160   | Method for extraction of vanadium from waste SCR catalyst and preparation of activated titanium silicon tungsten powder | 2017 | Shi et al., 2017b              |
| CN106450371   | Method for recycling failed vanadium electrolyte                             | 2017 | Chen, 2017                     |
| CN106244808   | Method for recycling vanadium from powdery vanadium-containing material      | 2016 | Zhang et al., 2016b             |
| CN106319230   | Method for recycling metal titanium, vanadium and tungsten from waste SCR catalyst through dry method | 2017 | Fu, 2017                      |
| CN106277043   | Method for extracting and separating metallic oxide from flue gas denitration catalyst | 2017 | Gao et al., 2017a              |
| CN106048227   | Method for efficiently recycling vanadium in vanadium-containing underflow slag | 2016 | Wan et al., 2016               |
| CN106011502   | Method for recycling vanadium, cobalt and nickel                             | 2016 | Yin, 2017                      |
| CN106011503   | Method for recycling tungsten, vanadium and titanium from SCR waste catalysts | 2016 | Ding, 2016                    |
| CN106011472   | Method for recycling vanadium in waste SCR denitration catalyst through reductive organic acid | 2016 | Qi et al., 2016               |

(continued on next page)
| Patent number | Patent title                                                                 | Year | Reference |
|---------------|-------------------------------------------------------------------------------|------|-----------|
| CN105986123   | Method for extracting vanadium from vanadium-containing waste catalyst         | 2016 | Li et al., 2016a |
| CN105980873   | Method for recycling vanadium, tungsten and titanium from waste SCR            | 2016 | Liu et al., 2016c |
| CN105909945   | Recycling treatment method for wasted SCR catalyst                             | 2016 | Zhao and Ming, 2016 |
| CN105861829   | Method for separating vanadium and chromium solution and recycling vanadium    | 2016 | Li et al., 2016d |
| CN105838885   | Comprehensive recycling method for waste SCR catalysts                         | 2016 | Xia et al., 2016 |
| CN105648220   | Technology for recycling vanadium from hydrogenation tail oil of suspended bed | 2016 | Deng et al., 2016 |
| CN105732319   | Process for purifying and treating vanadium-containing wastewater in advanced | 2016 | He et al., 2016 |
| CN105671306   | Method for separating iron, vanadium and titanium in vanadic titanomagnetite   | 2016 | Qin et al., 2016 |
| CN105714131   | Method for separating and extracting vanadium and chromium from same solution  | 2016 | Li et al., 2016e |
| CN1056797964  | Method for selectively reducing, separating and recycling vanadium and chrome  | 2016 | Wang et al., 2016a |
| CN105420519   | Method for extracting vanadium and chromium from materials containing vanadium| 2016 | Wang et al., 2016b |
| CN105331822   | Method for recycling vanadium in waste containing vanadium                     | 2016 | Zhang et al., 2016c |
| CN105331816   | Method for recycling vanadium and silicon through asynchronous conversion     | 2016 | Li et al., 2016 |
| CN105296762   | Method for preparing vanadium liquid through vanadium oxide industrial waste   | 2016 | Chen et al., 2015 |
| CN105274344   | Method for recycling vanadium and molybdenum from waste petroleum catalyst     | 2016 | Liu, 2016 |
| CN105251525   | Recycling method of vanadium-containing waste FCC (fluid catalytic cracking)   | 2016 | Guo and Liu, 2016 |
| CN105217685   | Method and apparatus for recycling vanadium pentoxide from waste flue gas     | 2016 | Su et al., 2016 |
| CN105124690   | Method for recycling vanadium and silicon simultaneously from silicious type   | 2015 | Xing et al., 2015 |
| CN10512678    | Method for magnetically separating and smelting chromium-iron alloy by vanadium | 2015 | Li et al., 2015a |
| CN105087961   | Method for efficiently recycling vanadium, iron and titanium in vanadium-titanium | 2015 | Hongzhi, 2015 |
| CN105087933   | Method for separating vanadium and chromium from vanadium mixed solution       | 2015 | Li et al., 2015b |
| CN104928464   | Method for extracting valuable metal in vanadium containing material by        | 2015 | Zhang et al., 2015a |
| CN104831075   | Method for separating and purifying vanadium and molybdenum of waste          | 2015 | Lin et al., 2015 |
| CN10469328    | Method of preparing ferric vanadate from residue of aluminium powder vanadium  | 2015 | Zhang et al., 2015b |
| CN104611564   | Method for preparing vanadium and chromium from vanadium and chromium          | 2015 | Li et al., 2015a |
| CN104495873   | Method for separating vanadium and tungsten metals from waste SCR              | 2015 | Wang et al., 2015b |
| TW201516156   | Method for separating vanadium and tungsten from waste select disarray         | 2015 | Chen et al., 2015 |
| CN104386883   | Method for separating and recycling vanadium and chromium from vanadium       | 2015 | Wang et al., 2015b |
| CN104195342   | Method for recycling vanadium pentoxide in waste SCR (Selective Catalytic     | 2014 | Li et al., 2014a |
| CN104178638   | Method for separating and recycling vanadium and chromium from vanadium         | 2014 | Wu et al., 2014a |
| CN104178637   | Method for separating and recycling vanadium and chromium from vanadium-chrome| 2014 | Wu et al., 2014b |
| CN104125698   | Recycling method for vanadium-nitrogen alloy waste materials                    | 2014 | Guangkai, 2014 |
| CN104099576   | Recycling method for waste denitration catalyst                                | 2014 | Lin et al., 2014 |
| CN104086032   | Method for recycling vanadium precipitating wastewater                         | 2014 | Chen et al., 2014 |
| CN104064786   | Method for recovering metals from vanadium slag                                | 2014 | Zhaqian, 2014 |
| CN104017999   | Vanadium extraction method for converter vanadium slags                         | 2014 | Yu et al., 2014 |
| CN103924096   | Method for recycling vanadium-chromium resources                              | 2014 | Wu et al., 2014c |
| CN103898330   | Method for comprehensively recycling such valuable metals as iron, aluminium,  | 2014 | Dong et al., 2014 |
| CN103898329   | Method for separating vanadium from vanadium slag through manganese            | 2014 | Yin et al., 2014 |
| CN103894977   | Method for recycling waste SCR (Selective Catalytic Reduction)                 | 2014 | Li et al., 2014b |
| CN103849765   | Method for precipitation separation and recovery of chromium and vanadium     | 2014 | Ning et al., 2014b |
| CN103773956   | Method for separating and recycling vanadium and chromium                      | 2014 | Gang, 2014 |
| CN103740934   | Method for recycling chemical substances from industrial slag containing      | 2014 | Liu et al., 2014 |
| CN103526019   | Method for comprehensive recycle of vanadium, selenium and silver from        | 2014 | Jiang et al., 2014 |
| CN103409637   | A method of recycling vanadium from removed silicon slags                      | 2013 | Yang et al., 2013a |
| CN103434174   | Method for separating titanium, iron, vanadium and calcium from mixed         | 2013 | Zhang et al., 2013b |
| CN103276218   | Method for recycling vanadium from vanadium-containing electrolysis aluminum | 2013 | Zhou et al., 2013 |
| TW201232622   | Method for recycling metal oxide from denitration waste catalyst              | 2013 | Sun et al., 2013a |
| TW2012315815  | Method for recycling rare earth, vanadium and nickel from catalyst waste       | 2013 | Sun et al., 2013b |
| CN103111367   | Method for separating and recycling valuable substances of vanadium extraction | 2013 | Li et al., 2013 |
| CN103045868   | Recovery process of honeycomb type selective catalytic reduction (SCR)         | 2013 | Zhang et al., 2013a |
| CN102936039   | Recovery process of honeycomb type selective catalytic reduction (SCR)         | 2013 | Rui, 2013 |
| CN102925693   | A method for extracting metal in waste catalyst RDS / HDS by using acid        | 2013 | Yulog et al., 2013 |
| CN102899487   | Process for leaching vanadium out of stone coal by using oxidant and sulfuric | 2013 | Yan et al., 2013 |
| CN102876899   | Method for effectively separating vanadium and chromium from vanadium-leaching | 2013 | Li et al., 2013 |
| CN102876895   | Method for recycling vanadium and chromium from low-concentration pentavalent | 2013 | Yin et al., 2013a |
| CN102864318   | Method for recycling vanadium from acid vanadium-containing solution         | 2013 | Xing et al., 2013 |
| CN102732736   | Method for extracting vanadium from burning slag of stone coal vanadium mine    | 2012 | Ailiang and Jinjiao, 2012 |
| CN102676810   | Method for separating and recycling vanadium and chromium from vanadate-chrome | 2012 | Mingyu et al., 2012 |
| CN102616851   | Resource recycling method for 80 ferrovanadium slag                           | 2012 | Jian et al., 2012 |
| CN102586613   | Method for recycling vanadium from vanadium-containing steel slags             | 2012 | Lanjie and Ruguo, 2012 |
account. The study identified 143 inventions related to the waste exploitation for vanadium recovery (Table 17), mainly from: tailings, slags, spent catalysts, different kinds of industrial waste, industrial wastewater (or vanadium rich solutions which simulates real flows). The high number of patents proves the actual interest in the implementation of an urban mining strategy, with an increasing trend since 2011, for all the considered scraps (Fig. 10).

Around 92% of the gathered inventions was developed in China, whereas the remaining percentage is shared among Taiwan, USA, Great Britain, Hungary and South Korea. The reason could be the Chinese willpower to increase the already high vanadium primary production, around 53% of the whole market (EC, 2017b), with the supply from secondary raw materials.

The collected patents include matrices in which the metal target is combined with different metals: titanium, iron, chromium, manganese, tungsten, molybdenum, aluminum, silicon, cobalt, nickel, silver, selenium. Overall, the described processes include a pre-treatment, specific for the waste type. Usually, this preliminary step is followed by hydrometallurgical treatments for the vanadium extraction, mainly acid or alkaline leaching, at different conditions, irrespective of the starting matrix. A consecutive stage allows the vanadium recovery and the solvent extraction (combined with a precipitation) is one of the most common options to ensure the highest metal purity (Du et al., 2018; Li, H. et al., 2018; Shikun et al., 2010; Wang, Y. et al., 2017b; Xi et al., 2018; Xia et al., 2016; Zhang, T. et al., 2015).

Alternatively, this technique is replaced by a precipitation with ammonium salts followed by a calcination or roasting (Deng et al., 2016; Li, H.-Y. et al., 2016; Li, H. et al., 2016; Song et al., 2017d, 2017e, 2017f; Su et al., 2016; Wang, 2017a; Wang X. et al., 2015; Xing et al., 2013; Yan et al., 2013; Yang et al., 2017; Z. Yin et al., 2013; Yuan et al., 2017; Yue et al., 2010; Zhang, T. et al., 2018; Zhang, K. et al., 2018; Zibi et al., 2012c), or the addition of an oxidizing agent (Gao, X. et al., 2017; Jian et al., 2012; Li X. et al., 2015; Zhou et al., 2018) for the vanadium pentoxide production.

On the other hand, the adsorption by resins for the selective vanadium recovery was described for the treatment of both wastewater or metal rich synthetic solutions (He et al., 2016; Li, H. et al., 2015b; Li, W. et al., 2016; Mingyu et al., 2012; Yin, D. et al., 2013; Zibi et al., 2012a, 2012b) and spent catalysts (Sun et al., 2013b; Xia et al., 2017).

An additional study focused on the European Commission funded projects to better understand the research evolution over time. With this aim, the European Commission Cordis portal was used and the two keywords: “vanadium recycling” and “vanadium recovery” were selected (https://cordis.europa.eu/). Table 16 shows the research results, proving an interest which started in 1983 with an Italian task for the exploitation of different residues. The relevance of this topic continues until today, as confirmed by the ERA-MIN French project. Overall, the main waste targets for the vanadium recovery include the spent catalysts and the steel slags, in agreement with the study of patents.

### Table 17 (continued)

| Patent number | Patent title | Year | Reference |
|---------------|--------------|------|-----------|
| CN101921916   | Method for recycling metal oxide from waste flue gas desulfurization catalyst | 2010 | Yue et al., 2010 |
| CN101914695   | Method for recycling vanadium from vanadium ore containing high silicon and high carbon via wet process | 2010 | Shikun et al., 2010 |
| KR200901008981| Method for manufacture vanadium, molybdenum, aluminium oxide from desulfurization waste catalyst of an oil refinery | 2009 | Moon and Moon, 2009 |
| US2004028585  | Method for recycling spent lithium metal polymer rechargeable batteries and related materials | 2004 | Cardarelli and Dube, 2004 |
| KR20030065204 | Recycling method for recovering vanadium from waste containing vanadium | 2003 | Lee et al., 2003 |
| GB2370567    | Process for extracting precious metal from waste material | 2002 | Robinson and Bentley, 2002 |
| HU9600344    | Method for recycling of vanadium wastes | 1998 | Hoffmann et al., 1998 |
| GB956403     | Recovery of copper and vanadium from aqueous streams by ion-exchange | 1964 | Monsanto Chemicals, 1964 |

This publication is based upon work from COST Action CA15102 supported by COST (European Cooperation in Science and Technology): “Solutions for Critical Raw Materials Under Extreme Conditions (CRM-EXTREME)”, Working Group WG 4 – Value chain
Ailiang, C, Jinqiang, C, 2012. Method for extracting vanadium from burning slag of stone coal vanadium mine fluidized bed. CN102732736. 
Bai, C, 2017a. Blast furnace smelting method for vanadium-titanium magnetite. CN106755668. 
Bai, C, 2017b. Blast furnace smelting method of vanadium-titanium magnetite. CN106636506. 
Bauer, G., Güther, V., Hess, H., Otto, A., Roidl, O., Roller, H., Sattelberger, S., Köther-Becker, S., Beyer, T., 2017. Vanadium and Vanadium Compounds. Ullmann's Encyclopedia of Industrial Chemistry. 
Bedelova, Z., Akcil, A., Bedelova, Z., Anarbekov, K., Baikonurova, A., Tuncuk, A., 2016. A review on management and recycling of spent selective catalytic reduction catalyst. J. Environ. Chem. Eng. 5 (5), 4702–4706. 
Bellurians, L. De Wilde, E., Moelans, N., Verheken, K., 1985. Metal losses in pyrometallurgical operations - A review. Adv. Collid. Interface Sci. 255, 47–63. 
Biswas, R.K., Wakhara, M., Taniguchi, M., 1985. Recovery of vanadium and molybdenum from heavy oil desulfurization waste catalyst. Hydrometallurgy 14 (2), 219–230. 
Breit, G.N., 1992. Vanadium-resources in fossil fuels. In: DeYoung, J.J.H., (Ed.) Flow Studies for Recycling Metal Commodities in the EU and the Implementation of the Raw Materials Initiative. 
Buckingham, I., De Wilde, E., Moelans, N., Verbeken, K., 2018. Metal losses in redox flow batteries for the storage of renewable energy: a review. Renew. Sustain. Energy Rev. 29, 325–335. 
Ailiang, C, Jinqiang, C, 2012. Method for extracting vanadium from burning slag of stone coal vanadium mine fluidized bed. CN102732736. 
Akkil, A., Vegliò, F., Ferella, F., 2018. A review on management and recycling of spent selective catalytic reduction catalyst. J. Cleaner Prod. 246, 118990. 
Fischer, R.P., 1975. Vanadium resources in titaniferous magnetite deposits. United States Geological Survey, Professional Paper, Washington. 
Fritz, J.S., Abbink, J.E., 1962. Cation exchange separation of vanadium from metal. US Patent 3199745. 
Fu, S., 2017. Method for recycling metal titanium, vanadium and tungsten from waste SCR catalyst through dry method. CN106319230. 
Gang, S., 2014. Method for separating and recycling vanadium and chromium. CN105103956. 
Gao, J., Zhang, J., Wang, F., Wang, H., Lin, W., Yan, D., Qi, Y., 2018. Method for comprehensively recycling vanadium-titanium-series denitration spent catalyst. CN107940403. 
Gao, J., Jiang, T., Zhou, M., Wen, J., Li, X., Wang, Y., Xue, X., 2017a. Effect of microwave irradiation and conventional calcification roasting with calcium
hydroxide on the extraction of vanadium and chromium from high-chromium vanadium slag. Int. J. Miner. Process.
Gao, X., Zheng, C., Cen, K., Ni, M., Luo, Z., Song, H., Wu, W., Yu, H., Wang, C., Zhuo, J., 2017. Method for extracting and separating metallic oxide from flue gas denitration catalyst. CN106277043.
García, R., Galantone, R., 2002. A critical look at technological innovation typology and innovation: a literature review. J. Prod. Innov. Manag. 19, 110–122.
Gilligan, A., Nikolaou, N., 2020. The extraction of vanadium from titanomagnetites and other sources. Miner. Eng. 146, (October 2019) 106106.
Gomes, H.L., Jones, A., Rogerson, M., Greenway, G.M., Lisbona, D.F., Burke, I.T., Mayes, W.M., 2017. Recovery of recovery of vanadium from alkaline steel slag leachates with anion exchange resins. J. Environ. Manage. 187, 384–392.
Gonçalves, J.M., Ireno Da Silva, M., Angnes, L., Araki, K., 2020. Vanadium-containing EEG. A.K., Biswas, R.K., 2019. A study on the kinetics of extraction of Ti(IV) from sulphate medium by Cyanex 302. Sep. Purif. Technol. 221, 331–337.
Kelley, K.D., Scott, C.T., Polya, D.E., Kimball, B.E., 2017. Vanadium. In: Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply. In: Schulz, K.J., DeYoung, J.J.H., Seal II, R.R., Bradley, B.C. (Eds.), Professional Paper 1802 U. Reston, VA, p. 48.
Keränen, A., Leväväki, T., Salakka, A., Tankanen, J., 2015. Recovery of nickel and vanadium from ammonical industrial wastewater by ion exchange and adsorption on activated carbon. Water Treat. 53 (10), 2645–2654.
Khorif, S., Wahoudi, A., Reda, Y. 2001. Recovery of vanadium pentoxide from spent catalyst used in the manufacture of sulfuric acid. Polytechnichem. Eng. 45 (2), 131–137.
Kimi, H.-I., Moon, G., Choi, I., Lee, J.-Y., Jothi, R.K., 2018. Hydrometallurgical process development for the extraction, separation and recovery of vanadium from spent desulfurization catalyst bio-lease. J. Cleaner Prod. 187, 449–458.
Kim, J.W., Lee, W.G., Hwang, I.S., Lee, J.Y., Han, C., 2015. Recovery of tungsten from spent selective catalytic reduction catalysts by pressure leaching. J. Ind. Environ. Chem. 28, 77–78.
Kimi, 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 residue/desulfurization (RDS) catalyst using solvent extraction. J. Ind. Environ. Chem. 20 (6), 4457–4462.
Kiyonaga, E., Hinoki, K., Morita, K., Yoshikawa, T., Haruta, M., Toru, M., Mino, T., 2018. Method for recycling denitration catalyst. US20182089041.
Krutzler, T.R., Reisinger, H., Schindler, I., 2012. Ressourcenverbrauch der Industrie in Österreich. Analyse und Ausblick für die bedeutendsten Branchen und seltene Metalle. Umweltbundesamt GmbH, Vienna, Austria.
Lai, Y.D., Liu, J.C., 1997. Leaching behaviors of Ni and V from spent catalyst. J. Hazard. Mater. A 8 (5), 2171–2206.
Lanjie, L., Ruiguo, B., 2012. Method for recycling vanadium-containing steel slag. CN102586613.
Le, M.N., Lee, M.S., 2020. A review on hydrometallurgical processes for the recovery of valuable metals from spent catalysts and life cycle analysis perspective. Miner. Process. Extr. Metall. Rev. 00 (00), 1–20.
Lee, C.G., Lee, G.L., Park, M.H., Yang, D.H., 2003. Recycling method for recovering vanadium from waste vanadium slag. KR20030065024.
Li, H., Wu, H., Wang, H., Liao, W., 2018. Method for leaching metal in vanadium titanomagnetite through full acid method. CN108165741.
Li, D., Peng, S., Liu, B., Chen, Y., 2018. Recovery method for vanadium in oxygen-enriched acid roasting vanadium precipitation waste liquid. CN107739832.
Li, M., Liu, B., Zheng, S., Wang, S., Du, H., Dreisinger, D.B., Zhang, Y., 2017a. A cleaner vanadium extraction method featuring non-salt roasting and ammonium bicarbonate leaching. J. Cleaner Prod. 149, 206–217.
Li, M., Zheng, S., Liu, B., Wang, S., Dreisinger, D.B., Zhang, Y., Du, H., Zhang, Y., 2017b. A clean and efficient method for recovering vanadium from vanadium slag: nonsalt roasting and ammonium carbonate leaching processes. Miner. Process. Extr. Metall. Rev. 38 (4), 228–237.
Li, D., Wan, H., Lu, Y., Wang, L., Tian, W., Jia, L., 2017. Vanadium-containing waste recycling utilization method. CN107287493.
Li, L., Wang, H., Du, H., Zheng, S., Liu, B., Wang, S., 2017. Method for decomposing vanadium-containing steel slag through sodium bicarbonate for recycling vanadium. CN107255357.
Li, H.-Y., Wang, K., Hua, W.-Y., Yang, Z., Zhou, W., Xie, B., 2016a. Selective leaching of vanadium in calcification-roasted vanadium slag by ammonium carbonate. Hydrometallurgy 160, 18–25.
Li, H., Wu, W., Bao, W., Wang, Y., 2016. Method for extracting vanadium from vanadium-containing waste catalyst reductive organic acid. CN105966123.
Li, M., Li, Q., Li, Guo, J., Wang, Y., Yin, Z., Gao, B., Bang, Y., Yang, Y., 2016. Method for separating vanadium and chromium solution and recycling vanadium and chromium. CN105862736.
Li, W., Wang, J., Duan, L., 2016. Method for separating and extracting vanadium and chromium from same solution. CN105714131.
Li, H., Guo, C., Du, Z., Feng, Y., Yang, X., 2016. Method for recycling vanadium and silicon through asynchronous conversion of silicate vanadium ores. CN105331816.
Li, M., Peng, Y., Yang, Y., Zhou, Y., Fu, Z., Xiao, L., Gao, G., 2015. Method for magnetically separating and smelting chromium-iron alloy by vanadium extraction from vanadium-chromium slag and reduction of tailings. CN105112678.
Li, H., Zhang, M., Li, B., C., 2015. Method for separating and recovering chromium from the vanadium and chromium mixed solution. CN105087933.
Li, D., Lu, Y., Meng, X., Qi, J., Li, W., Feng, F., 2015. Recycling method for vanadium-chromium waste residues. CN104726715.
Li, X., Liu, Z., Wang, Y., Li, F., Wang, Z., 2015. Method for recycling metal oxides from waste SCR (selective catalytic reduction) catalyst. CN104611564.
Li, W., Yu, W., Zhang, Y., 2020. Method for separating and recovering vanadium and chromium by exchange and solvent extraction in recovering vanadium from sulfuric acid leach solutions of stone coal. Hydrometallurgy 131–132, 1–7.
Li, H., Li, S., Fang, S., Hao, B., Song, G., Dong, G., 2013. Method for separating and recycling valuable substances of vanadium extraction waste slag by superconduction high-gradient magnetic separation technology. CN101113167.
Li, H., Li, C., Fang, H., Wang, N., Wang, Y., Xie, B., 2013. Method for effectively separating and extracting vanadium and chromium from vanadium-leaching wastewater. CN102678699.
Li, X.-B., Wei, C., Wu, J., Li, C.-X., Li, M.-T., Deng, Z.-G., Xu, H.-S., 2012. Thermodynamics and mechanism of vanadium(IV) extraction from sulfamate media with D2EHPA, EHEHPA and CYANEX 272 in kerosene. Trans. Nodner. Met. Soc. China 22 (2), 461–466.
Li, X.-S., Xie, B., 2012. Extraction of vanadium from high calcium vanadium slag using direct roasting and soda leaching. Int. J. Miner. Metall. Mater. 19 (7), 595–598.

Li, X., Wei, C., Deng, Z., Li, M., Li, C., Fan, G., 2011. Selective solvent extraction of vanadium from a copper-nickel/molybdenum slag system by using a new phosphoric compound. Hydrometallurgy 105 (3), 359–363.

Li, G., Zeng, L., Xiao, L., Yang, Y., Zhang, Q., 2009. Completely removing vanadium from molybdenum/molybdate solution by utilizing ion exchange resins. Hydrometallurgy 98 (3), 287–290.

Lin, X., Liu, C., Pan, Y., Li, Z., 2015. Method for separating and purifying vanadium and molybdenum from vanadium-molybdenum SCF (selective catalytic reduction) catalyst. CN104593075.

Lin, D., Li, D., Song, B., Ma, S., Zhu, T., Wang, X., Yu, J., 2014. Recycling method for waste denitration catalyst. CN104099476.

Liu, C., Zhao, Y., Ma, S., Liu, C., Lu, W., Zou, L., Wang, X., Tang, S., 2016. Method for recycling vanadium, tungsten and titanium from wastewater SCF denitration catalyst. CN105950873.

Liu, Z., Li, Y., Chen, M., Nueurainematil, A., Du, J., Fan, X., Tao, C.-Y., 2016b. Enhanced leaching of vanadium slag in acidic solution by electro-oxidation. Hydrometallurgy 159–15.

Liu, J., Shan, H., Zhu, Y., Cai, L., Cui, W., Zhou, X., Wang, X., 2014. Method for recycling chemical substances from industrial slag containing vanadium, chromium, platinum and Mn. CN103740934.

Liu, G.Z., Sui, Z.T., 2002. The study of extracting vanadium and molybdenum from HDS spent catalyst. Compr. Ull. Miner. 4 (2), 39–41.

Lourenßens, K., Williams, J., Ahmadpour, F., Clemmer, R., Tazmin, S., 2019. Vanadium redox flow batteries: A comprehensive review. J. Storage Mater. 25 (June).

Lozano, L.J., Gods, O., Nee, C., 2003. Comparative study of solvent extraction of vanadium from sulphate solutions by primene 81R and amalane 336. Miner. Eng. 16 (3), 291–296.

Lu, Q., Chen, C., Zhang, Y., Dong, C., Yang, Y., 2014. Method for recycling vanadium pentoxide in waste SCF (Selective Catalytic Reduction) catalyst. CN104195342.

Magyar, M.J., 2009. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs09.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2008. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2008-vanad.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2007. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2007-vanad.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2006. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2006-vanad.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2005. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2005-vanad.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2004. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2004-vanad.pdf. (Accessed 19 March 2019).

Magyar, M.J., 2003. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/vanadmcs-2003-vanad.pdf. (Accessed 19 March 2019).

Marafi, M., Stanislaus, A., Furimsky, E., 2010. Handbook of Spent Hydroprocessing Catalysts Regeneration, Rejuvenation, Reclamation, Environment and Safety. vanadium/700303.pdf. (Accessed 19 March 2019).

Mazurek, K., 2013. Recovery of vanadium, potassium and iron from a spent HDS catalyst. Compr. Util. Miner. 4 (2), 39–41.

Nejad, D.G., Khanchi, A.R., Taghizadeh, M., 2018. Recovery of vanadium from ammonium molybdate solution using chelating ion exchange resins. Sep. Purif. Technol. 137, 65–70.

Ning, P., Wang, Q., Cao, H., 2017. System for recovering heavy metal from waste SCR catalysts and treatment method thereof. CN106947864.

Ning, P., Lin, X., Cao, H., Zhang, Y., 2014. Selective extraction and deep separation of V(V) and Cr(VI) in the leaching solution of chromium-bearing vanadium slag with primary amine LK-N21. Sep. Purif. Technol. 137, 109–115.

Ning, P., Sun, G., Cao, H., Zhang, Y., 2014b. Method for precipitation separation and recovery of chromium and vanadium in chromium-vanadium-sulfonate solution. CN103827675.

Nitta, N., Wu, F., Lee, J.T., Yushin, G., 2015. Li-ion battery materials: present and future. Mater. Today 18 (5), 252–264.

Noori, M., Rashchi, F., Babakhani, A., Vahidi, E., 2014. Selective recovery and separation of nickel and vanadium in sulfamate media using mixtures of D2EHPA and Cyanex 272. Sep. Purif. Technol. 136, 265–273.

Ognyanova, A., Ozturk, A.T., De Michielis, L., Ferella, F., Taglieri, G., Akci, A., Veglio, F., 2009. Metal extraction from spent sulfuric acid catalyst through alkaline and acid leaching. Hydrometallurgy 100 (1–2), 20–28.

Okudan, M.D., Akici, A., Tuncuk, A., Deveci, H., 2015. Effect of parameters on vanadium recovery from by-products of the Bayer process. Hydrometallurgy 152, 72–83.

Parasuraman, A., Lim, T.M., Menicas, C., Skyllas-Kazacos, M., 2013. Review of material research and development for vanadium redox flow battery applications. Electrochem. Acta. 101, 27–40.

Polyak, D.E., 2014. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2014-vanad-2014-vanad.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2015. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2015-vanad-2015-vanad.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2016. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2016-vanad-2016-vanad.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2017. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2017-vanad-2017-vanad.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2018. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/mcs-2018-vanad-2018-vanad.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2019. Molybdenum. https://minerals.usgs.gov/minerals/pubs/commodity/molybdenum/mcs-2019-molyb.pdf. (Accessed 19 March 2019).

Polyak, D.E., 2020. Molybdenum. https://minerals.usgs.gov/minerals/pubs/commodity/molybdenum/mcs-2020-molyb.pdf. (Accessed 19 March 2019).

Prashanth, L., Kattapagari, K., Chitturi, R., Baddam, V., Prasad, L., 2015. A review on the usage of polyoxovanadates [V34O82]10− with primary amine LK-N21. Sep. Purif. Technol. 137, 65–70.

Ray, A.K., Goswami, B., Raj, A., Singh, M.P., 2013. Studies on pyrometallurgy of vanadium bearing iron, steel and slag. J. Metall. Mater. Sci. 55 (2), 99–111.

Razavi, S.M., Haghatalab, A., Khanchi, A.R., 2017. Solvent extraction and selective separation of vanadium (V) from an acidic sulfate solution using 2-Ethyl-1-Hexanol. Sep. Purif. Technol. 188, 358–366.

Razavi, S.M., Haghatalab, A., Khanchi, A.R., 2018. Thermodynamic modeling of the solvent extraction equilibrium for the recovery of vanadium (V) from acidic solution by ion exchange. Hydrometallurgy 136, 65–70.

Qin, J., Liu, G., Li, Z., Qi, Q., 2016. Method for separating silicon from vanadium and titanium in vanadic titanomagnetite. CN105671306.
sulfate solutions using Di-(2-ethylhexyl) phosphoric acid. Fluid Phase Equilib. 474, 20–31.

Reese, R.G., 2002. Vanadium. https://minerals.usgs.gov/minerals/pubs/commodity/vanadium/.

Shi, Q., Zhang, Y., Huang, J., Liu, T., Liu, H., Wang, L., 2017a. Synergistic solvent extraction of vanadium from pentoxide using acid diethylenetriamine. J. Cleaner Prod. 152, 202–224.

Seargeant, L.E., Stinson, R.A., 1979. Inhibition of human alkaline phosphatases by vanadium/700398.pdf. (Accessed 19 March 2019).

Shikun, P., Bake, L., Qiming, G., Xinglin, Y., Quan, Z., Xun, X., 2010. Method for treating vanadium extraction tailings. CN102491419.

Song, W., Wang, J., Li, H., Cao, Z., Wang, Q., Wu, D., 2017a. Method and system for removing phosphorus and extracting vanadium from high-calcium and high-phosphorus vanadium slag. CN106756159.

Song, W., Wang, J., Li, H., Cao, Z., Wang, Q., Wu, D., 2017b. Method and system for treating vanadium extraction tailings. CN106957963.

Sun, Y.-L., Tsai, M.-Z., Liu, Y.-H., 2013b. Method for recycling rare earth, vanadium and nickel from catalyst waste. TW201319515.

Splettostossl, W., Tkaczyk, A.H., Bartl, A., Amato, A., Lapkovskis, V., Petranikova, M., 2018. Sustainability evaluation of essential critical raw materials: cobalt, niobium, tungsten and rare earth elements. J. Phys. D Appl. Phys. 51, 203001.

Su, J., Jin, Y., Sun, L., Li, W., 2016. Method for extracting phosphorus and removing phosphorus from high-calcium and high-phosphorus vanadium slag. CN106756121.

Sui, J., Jin, Y., Sun, L., Li, W., 2016. Method and apparatus for recycling vanadium pentoxide from waste flue gas denitration catalyst. CN105217685.

Song, W.-S., Ming-zhe, T., Liu, Y.-H., 2013a. Method for recycling metal oxide from waste SCR catalyst containing tungsten, vanadium and titanium. CN106498165.

Survey, U.S.G., 2016. Historical statistics for mineral and material commodities in the United States (2016 version). In: Kelly, T.D.M., G.R.(Ed.), Historical statistics for mineral and material commodities in the United States; U.S. Geological Survey Data Series 140.

Takavoli, M.R., Dreisinger, D.B., 2014. Separation of vanadium from iron by solvent extraction using acidic and neutral organophosphorus extractants. Hydrometallurgy 141, 17–23.

Tkaczyk, A.H., Bartl, A., Amato, A., Lapkovskis, V., Petranikova, M., 2018. Sustainability evaluation of essential critical raw materials: cobalt, niobium, tungsten and rare earth elements. J. Phys. D Appl. Phys. 51, 203001.

Wang, L., Zhang, G., Guan, W., Zeng, L., Zhou, Q., Xia, Y., Wang, Q., Li, Q., Cao, Z., 2018. Complete removal of trace vanadium from ammonium tungstate solutions by solvent extraction. Hydrometallurgy 179, 268–273.

Wang, R., 2017a. Method of recycling component substances of waste SCR denitration catalyst at low cost. CN104714600.

Wang, R., 2017b. Method of recycling component substances in a waste SCR denitration catalyst. CN107416904.

Wang, X., Wang, M., Meng, Y., 2017a. Method for extracting vanadium and chromium from vanadium/chromium waste catalyst. CN106938377.

Wang, X., Wang, M., Meng, Y., 2017b. Method of recycling component substances in a waste SCR denitration catalyst. CN106945973.

Wang, X., Wang, M., Wang, X., Wang, M., Meng, Y., 2017a. Method for extracting vanadium and chromium from vanadium/chromium waste catalyst. CN106938377.

Wang, X., Wang, M., Meng, Y., 2017b. Method of recycling component substances in a waste SCR denitration catalyst. CN104714600.

Wang, X., Wang, M., Meng, Y., 2017a. Method for extracting vanadium and chromium from vanadium/chromium waste catalyst. CN106938377.

Wang, X., Wang, M., Meng, Y., 2017b. Method of recycling component substances in a waste SCR denitration catalyst. CN104714600.
Yang, Z., Li, H.-Y., Yin, X.-C., Yan, Z.-M., Yan, X.-M., Xie, B., 2014b. Leaching kinetics

Yang, K., Zhang, X., Tian, X., Yang, Y., Chen, Y., 2010. Leaching of vanadium from

Xu, X., Xiong, F., Meng, J., Wang, X., Niu, C., An, Q., Mai, L., 2020. Vanadium-based

Xiao, Q., Chen, Y., Gao, Y., Xu, H., Zhang, Y., 2010. Leaching of silica from vanadium-

Wu, Z., Jiang, L., Fu, Z., Gao, G., Peng, Y., 2014a. Method for separating and recycling vanadium and chromium from vanadium leaching reduction slags. CN104178638.

Wu, Z., Peng, Y., Fu, Z., Gao, W., Wang, Y., 2014b. Method for separating and recycling vanadium and chromium from vanadium leaching reduction slags. CN104178638.

Wu, K., Wang, Y., Wang, X., Wang, S., Liu, B., Zhang, Y., Du, H., 2018. Co-extraction of vanadium and chromium from high chromium containing vanadium slag by low-pressure liquid phase oxidation method. J. Chem. Prod. Proc. 203, 873–884.

Xi, X., Chen, J., Ma, L., Nie, Z., 2018. Method for recycling tungsten and vanadium from waste SCR denitration catalyst. CN107699659.

Xia, Q., Yang, X., Wu, F., Fan, M., Zhao, C., 2017. Method for efficiently extracting vanadium and tungsten from waste SCR denitration catalyst. CN106636646.

Xia, Q., Zhang, C., Yang, X., Wu, F., Fan, M., 2016. Comprehensive recycling method for waste SCR catalysts. CN105838885.

Xiang, J., Huang, Q., Lv, X., Bai, C., 2018. Extraction of vanadium from converter slag by two-step sulfuric acid leaching process. J. Cleaner Prod. 170, 1089–1101.

Xiao, Q., Chen, Y., Gao, Y., Xu, H., Zhang, Y., 2010. Leaching of silica from vanadium-bearing steel slag in sodium hydroxide solution. Hydrometallurgy 104 (2), 216–221.

Xie, T., Tian, X., Dong, T., Yin, H., He, J., 2018. Method for recycling waste SCR denitration catalyst. CN107979010.

Xie, X., Ning, S., She, Z., Wu, H., Liu, J., Wen, C., Feng, Z., Wang, W., 2015. Method for recycling vanadium and silicon simultaneously from siliceous type vanadium ore. CN104894318.

Xing, N., Ning, S., She, Z., Meng, Z., Li, Z., Liu, J., Chen, W., Huang, Z., Feng, Z., Wang, H., Zhao, Q., Wang, W., Wu, J., 2013. Method for recycling vanadium from acid vanadium-containing solution containing silicon and phosphorus. CN102864318.

Xu, X., Xiong, F., Meng, J., Wang, X., Niu, C., An, Q., Mai, L., 2020. Vanadium-based nanomaterials: a promising family for emerging metal-ion batteries. Adv. Funct. Mater. 1904398, 1–36.

Xue, X., Teng, A., Jiang, T., Yang, S., 2018. Method for recycling chromium and vanadium from chromium and vanadium containing slags. CN108048668.

Xue, X., Gao, Z., Cheng, G., Teng, A., Yang, H., Jiang, T., Duan, P., Zhou, X., 2017. Low-gravity calcination of vanadium-containing titanium magnetite sodium treatment oxidation-leaching vanadium extracting method. CN106995798.

Yan, W., Hua, J., Gao, F., Cai, J., He, X., 2013. Process for leaching vanadium out of stone coal by using oxidant and sulfuric acid. CN102899487.

Yang, S., Fang, J., Wang, J., Wang, J., 2017. Method for recycling vanadium from waste catalyst containing molybdenum and vanadium and method for preparing vanadium pentoxide. CN107012331.

Yang, X., Zhang, Y., Bao, S., Shen, C., 2016. Separation and recovery of vanadium from vanadium leaching solution of the vanadium as coal by solvent extraction using trialkylamine. Sep. Purif. Technol. 164, 49–55.

Yang, H., Mao, L., Xue, X., 2014a. Separation and recovery of chromium and vanadium from reduced vanadium-chromium precipitate by calcinations-Hydrometallurgy. Chem. Eng. J. 65 (3), 948–953.

Yang, K., Zhang, X., Tian, X., Yang, Y., Chen, Y., 2010. Leaching of vanadium from chromium residue. Hydrometallurgy 103 (1), 7–11.

Yang, Z., Li, H.-Y., Yin, X.-C., Yan, X.-M., Yan, X.-M., Xie, B., 2014b. Leaching kinetics of calcination roasting vanadium slag with high CaO content by sulfuric acid. Int. J. Miner. Process. 133, 105–111.

Yaroshkevich, A.A., 2006. Abundances of chemical elements in the Earth’s crust. Geochim. Int. 44 (1), 48–55.

Ye, P., Wang, X., Wu, M., Fan, Y., Xiang, X., 2012. Recovery of vanadium from stone coal leaching solution by coprecipitation, alkaline roasting and water leaching. Hydrometallurgy 117–118, 108–115.

Ye, G., Burström, E., Kuha, M., Pirtt, J., 2003. Reduction of steel-making slags for recovery of valuable metals and oxide materials. Scand. J. Metall. 32 (1), 7–14.

Yin, Z., 2017. Method for recycling vanadium, cobalt and nickel. CN106011502.

Yin, Z., Chen, X., Gao, C., Li, Q., 2014. Method for extracting vanadium from vanadium slag through manganese roasting. CN103898329.

Yin, D., Peng, Y., Fu, Z., He, G., Wao, C., Shen, B., 2013. Method for recycling vanadium and vanadium from low-concentration pentavalent vanadium and hexavalent chromium mixed liquor. CN102876895.

Yin, Z., Sun, Z., Gao, G., Wu, Z., Du, G., 2013. A method of recycling vanadium from removed silicon slag. CN103069033.

Yu, B., Sun, Z., Xian, Y., Peng, Y., Tang, H., Chen, H., Danfeng, Y., Du, G., Jinh, Wang, T., 2014. Vanadium extraction method for converter vanadium slag. CN103112221.

Yu, Z., Zhi, Z., Li, H., Shi, Z., 2014. Method for recycling high-purity ammonium vanadate through low-temperature precipitation. CN107503352.

Yue, Z., Sheng, H., Yang, Z., 2010. Method for recycling metal oxide from waste flue gas desulfurization catalyst. CN101921916.

Yulong, S., Yonghao, L., Mingzhe, C., 2013. A method for extracting metal in waste catalyst RDS/HDS by using acid leaching. CN102925963.