



Vanadium sustainability in the context of innovative recycling and sourcing development

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Vanadium sustainability in the context of innovative recycling and sourcing development



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ABSTRACT

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.

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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 1.34·10⁹ 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 1
Supply risk of selected critical elements and their concentration in the upper continental crust, Earth's crust, and seawater.

Element	Supply risk*	Upper continent EC,al crust*	Earth's crust [ppm]**	Seawater**
	[-]		[ppm]	
In	2.4	0.06	0.25	0.10
Bi	3.8	0.16	0.009	60
Ta	1.0	0.9	2.5	<2.50
Ge	1.9	1.4	1.4	5.00
W	1.8	1.9	1.3	10
Be	2.4	2.1	3.8	0.21
As	-	4.8	1.7	1200
Hf	1.3	5.3	1	3.40
Nb	3.1	12	20	<5.00
Co	1.6	17	18	1.20
Ga	1.4	17	19	1.20
V	1.6	97	90	2,000

* threshold for criticality: ≥ 1.0 ; (EC, 2017a).

* (Rudnick and Gao, 2003).

** (Yaroshevsky, 2006).

** (Haraguchi et al., 2003).

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	$K_2(UO_2)_2(V_2O_8) \cdot 1 - 3H_2O$	5+	About 20	USA (Colorado, Utah, New Mexico, Arizona), Australia, Kyrgyzstan	Anonymous, 2001–2005a
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$	5+	About 3	USA (Colorado, New Mexico, Utah), Germany, Austria, Czech Republic, UK	Anonymous, 2001–2005b
Corvusite	$(Na,Ca,K)_x(V^{5+},V^{4+},Fe^{2+})_8O_{20} \cdot 4H_2O$ ($x = 0.8$ to 1.2)	4+, 5+	75–85	USA (Utah, Colorado, Arizona), Gabon, Kazakhstan	Anonymous, 2001–2005c
Descloizite	$PbZn(VO_4)(OH)$	5+	About 23	Argentina, Mexico, USA (Arizona, New Mexico, Nevada), Namibia, Zambia, Congo Republic, Iran, Austria, Slovenia, Portugal	Anonymous, 2001–2005d
Doloresite	$H_8V_6O_{16}$	4+, 5+	78–87	USA (Colorado, Utah, New Mexico, Arizona, Wyoming), Australia, Argentina	Anonymous, 2001–2005e
Francevillite	$(Ba,Pb)(UO_2)_2(V_2O_8) \cdot 5H_2O$	5+	About 19	Gabon, Congo, Zimbabwe, France, Germany, England, Kyrgyzstan, Canada, USA (Pennsylvania)	Anonymous, 2001–2005f
Hewettite	$CaV_6O_{16} \cdot 9H_2O$	4+, 5+	About 71	Peru, USA (Colorado, Utah, Arizona, Nevada, South Dakota, Arkansas), Kazakhstan	Anonymous, 2001–2005g
Montroseite	$(V^{3+},Fe^{2+},V^{4+})O(OH)$	3+, 4+	10–90	USA (Colorado, Utah, Arizona, New Mexico, South Dakota), Czech Republic, Argentina, Gabon, China	Anonymous, 2001–2005h
Mottramite	$PbCu(VO_4)(OH)$	5+	21 – 22	England, USA (Arizona, New Mexico, Nevada), Chile, Namibia, Zambia	Anonymous, 2001–2005i
Paramontroseite	VO_2	4+	67–73	USA (Colorado, Utah, Arizona, New Mexico, South Dakota), Czech Republic, Argentina, Gabon	Anonymous, 2001–2005j
Pascoite	$Ca_3V_{10}O_{28} \cdot 17H_2O$	5+	65–66	Peru, Argentina, USA (Colorado, Arizona, New Mexico)	Anonymous, 2001–2005k
Patronite	VS_4 or $V(S_2)_2$	4+ or 5+	28*	Peru	Allmann et al., 1964; Anonymous, 2001–2005l; Rout et al., 2013 Anonymous, 2001–2005m
Roscoelite	$K(V^{3+},Al;Mg)_2AlSi_3O_{10}(OH)_2$	3+	About 20	USA (California, Colorado, Oregon, Arizona, Nevada), Japan, Australia, Fiji Islands, Czech Republic, Gabon	Anonymous, 2001–2005n
Tyuyamunite	$Ca(UO_2)_2(V_2O_8) \cdot 5 - 8H_2O$	5+	About 19	Kyrgyzstan, England, USA (New Mexico, Colorado, Utah, Arizona, Nevada), Mexico, Argentina, Israel	Anonymous, 2001–2005n
Vanadinite	$Pb_5(VO_4)_3Cl$	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 mainly 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 (Fe_3O_4) and hematite (Fe_2O_3) but also in rutile (TiO_2) and perovskite ($CaTiO_3$) deposits are possible sources (Fischer, 1975). Usually vanadium in titaniferous magnetite deposits is concentrated as a solid solution in magnetite-ulvospinel, where V^{3+} has replaced Fe^{3+} (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).

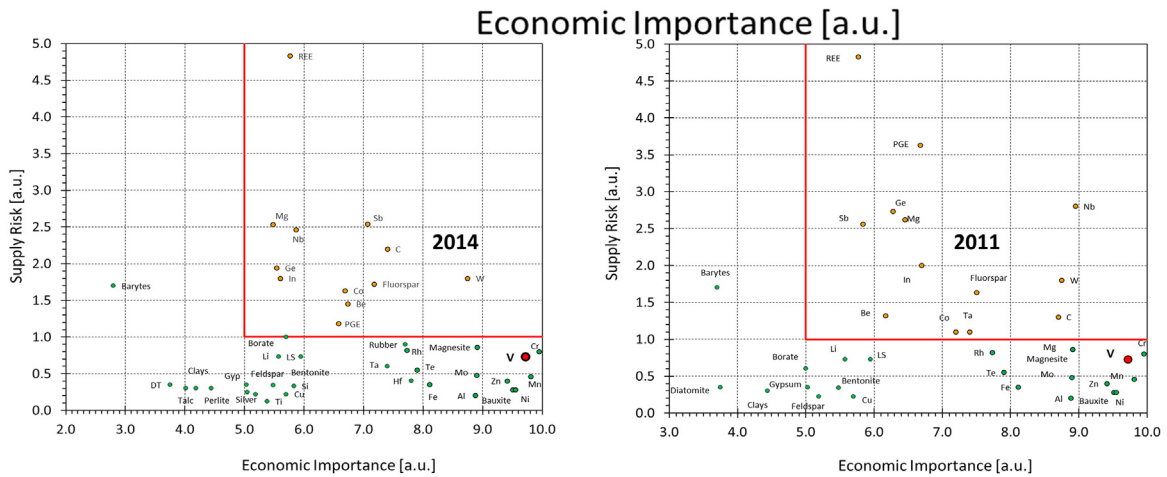
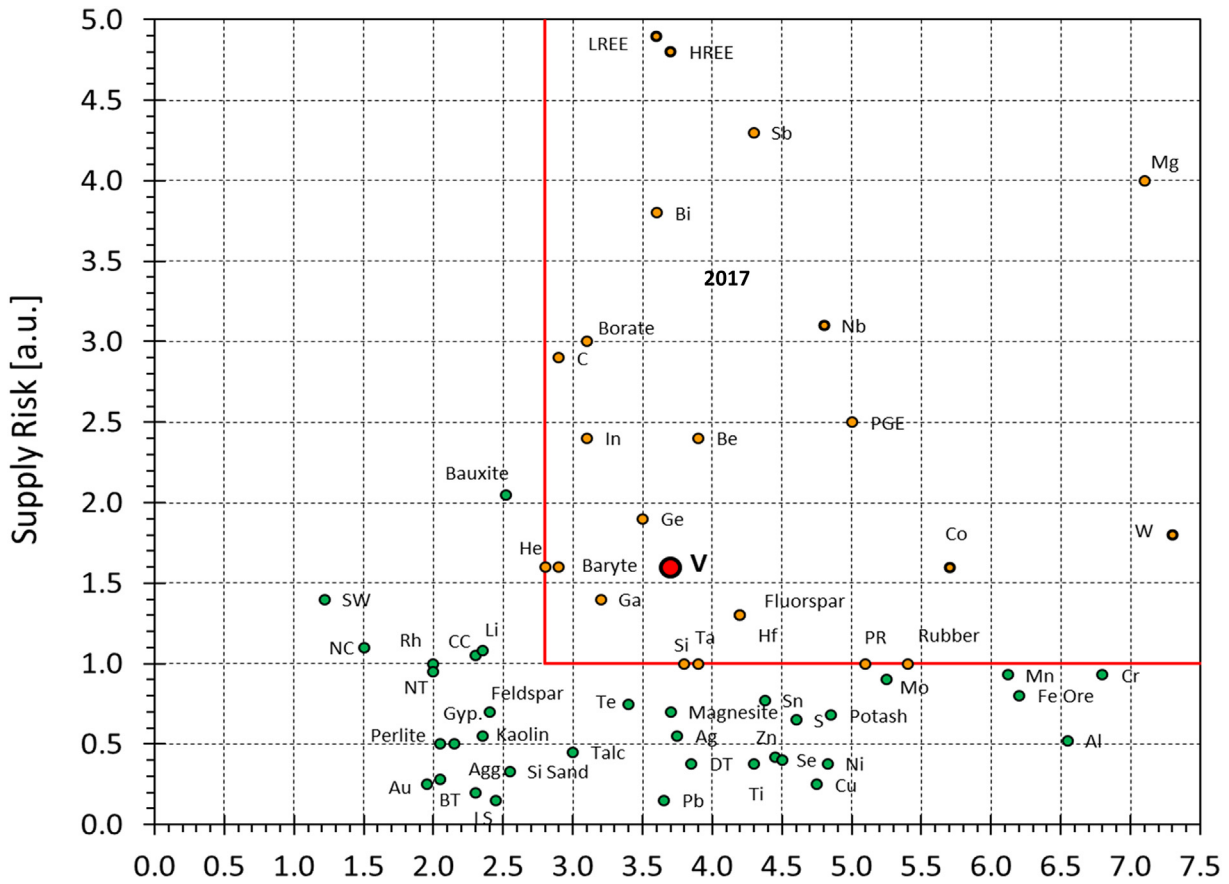
2.2. Vanadium in the EU

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 V_2O_5 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-



a.u.....arbitrary units
 Agg.....Aggregates
 BT.....Bentonite
 C.....Natural graphite
 CC.....Coking Coal
 DT.....Diatomite
 Gyp.....Gypsum
 LREE... Light Rare Earth Elements
 HREE... Heavy Rare Earth Elements
 LS.....Limestone
 NC..... Natural Cork
 NT..... Natural Teak
 PGE.....Platinum group metals
 (Ru, Rh, Pd, Os, Ir, Pt)
 PR.....Phosphare Rock
 Rubber Natural Rubber
 Si Sand Silicon Sand
 SW..... Sapele Wood

Fig. 1. EU criticality assessment of 2011, 2014 and 2017 (EC, 2011, 2014b, 2017b).

Table 3
 European Union's vanadium production in the period 2010 to 2014 (EC, 2017a).

Process	EU production volume [t]	Main EU countries
V ore extraction	0	–
Pentoxide production	1650	BE, UK, NL, DE
Ferrovandium production	2000	CZ

sidered. Ferrovandium (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 4
Vanadium imports into the EU in 2014 (Brown, 2016).

Country	Product group [t]			Total
	Vanadiferous residues	Pentoxide	Metal (ferrovanadium)	
AT	46,000	1754	–	47,754
BE	–	26	–	26
CZ	–	9202	–	9202
FR	–	660	94	754
DE	–	400	50	450
IT	–	304	–	304
NL	–	3465	333	3798
ES	–	36	–	36
UK	–	–	168	168
Total	46,000	15,847	645	62,492

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 converted into ferrovanadium which is primarily used for steel alloying (Hassan, 2003; Krutzler et al., 2012). Vanadium containing steel grades are in particular used for tool steels (DIN, 2018):

- alloyed cold worked steels, vanadium concentration between 0 and 1%;
- hot-working steels, vanadium concentration between 0.05 and 2.1%, and
- high-speed steels, vanadium concentration between 0.9 and 4.2%.

“Voestalpine” is an Austrian based company and has a worldwide leadership in tool steel and a leading position in high-speed steel (Voestalpine, 2016). The high-performance metals division, responsible for the production of tool steel, had a revenue of 2.7 billion € in 2016/17. The divisional revenues are mainly based in EU (49%) and third countries (47%), whereas Austria plays a minor role (4%).

It is, however, clear that the exports, inside and outside the EU, of tool steels will not account for vanadium exports in the statistics but amongst steel. Nevertheless, it is clear that most of the imported vanadiferous residues to Austria will finally end up in tool steels.

2.3. Markets

Vanadium is mainly used as alloying element for steel. As demonstrated by Table 6 different categories of steel alloys domi-

Table 5
Vanadium exports from the EU in 2014 (Brown, 2016).

Country	Product group		Total
	Pentoxide	Metal (ferrovanadium)	
BE	3	–	3
DE	–	369	369
IT	–	477	477
NL	314	–	314
ES	102	–	102
Total	419	846	1,265

Table 6
End uses and substitution index for vanadium (EC, 2014b).

Product group	Share [%]	Substitutability
Full alloy (incl. tool steel)	32	0.5
HSLA steel (long products)	25	0.3
HSLA steel (plate)	18	0.3
Carbon steel	13	0.7
Titanium alloy	5	1.0
Chemicals	4	0.3
Other iron & steel	2	0.5
Other (mainly batteries)	1	0.5

nate 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.

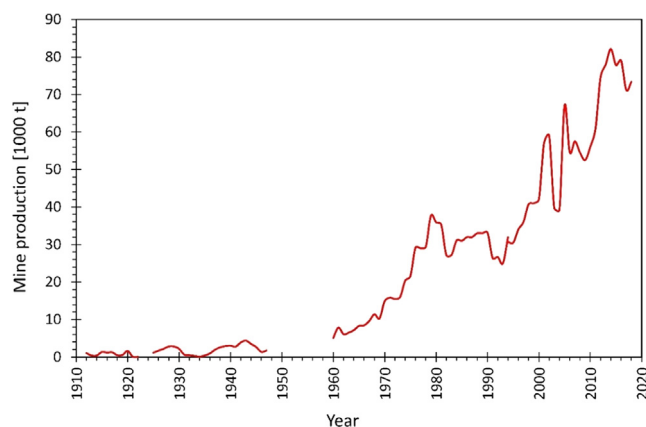


Fig. 2. World mine production of vanadium in the period 1912 to 2018 (no data available 1923/1924 and 1948–1959), data for 1910–2015 (Survey, 2016), for 2016 (Polyak, 2018), for 2017 (Polyak, 2019) and estimate for 2018 (Polyak, 2019).

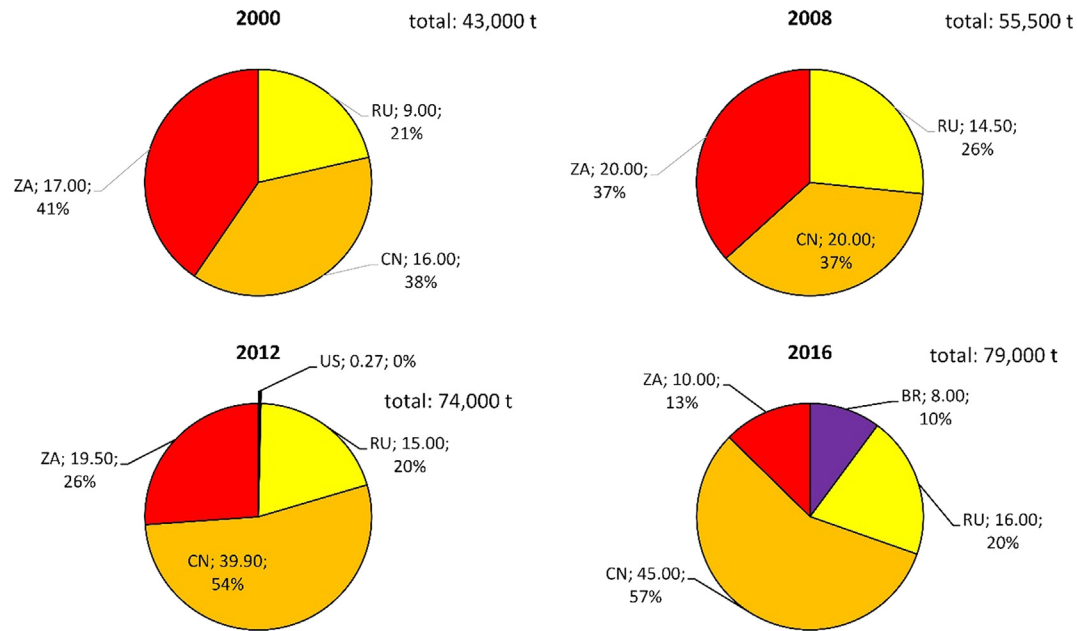


Fig. 3. World mine production of vanadium by country in 1,000 t and the share in %; data retrieved from: 2000 (Reese, 2002); 2008 (Polyak, 2010); 2012 (Polyak, 2014); 2016 (Polyak, 2018).

Table 7 compares data from the U.S. Geological Survey (USGS) and the British Geological Survey (BGS). There are certain deviations between the references. In particular the USGS reports a significant decrease in mine production for South Africa from 21,000 t in 2015 (Polyak, 2017) to 9100 t in 2017 (Polyak, 2019) whereas according to the BGS the decrease is only moderate from 21,552 t in 2014 to 18,000 t 2016 and 2017 (Brown, 2018). Regarding the world production the sources report a gap of 13,000 t (73,000 t vs. 86,000 t) in 2017 (Brown, 2018; Polyak, 2019). However, 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 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).

$$\text{Time to depletion [a]} = \frac{\text{Reserves [t]}}{\text{Mine production} \left[\frac{\text{t}}{\text{a}} \right]} \quad (2.5.1)$$

Table 7

Vanadium mine production (2013 – 2017) in t per country according to the U.S. Geological Survey (USGS) and British Geological Survey (BGS).

Country*	Source**	2013	2014	2015	2016	2017
CN	USGS	41,000	45,000	42,000	45,000	40,000
	BGS	45,000	48,000	45,000	45,000	43,000
RU	USGS	15,000	15,100	16,000	16,000	18,000
	BGS	14,403	15,125	16,196	16,886	18,636
ZA	USGS	21,000	21,000	14,000	10,000	9,100
	BGS	21,397	21,582	17,788	18,000	18,000
US	USGS	591	–	–	–	–
	BGS	591	–	–	–	–
AU	USGS	400	–	–	–	–
	BGS	–	–	–	–	–
BR	USGS	–	1,030	5,800	8,000	5,210
	BGS	–	578	3,254	4,461	5,206
KZ	USGS	–	–	–	–	–
	BGS	1,000	1,000	1,000	1,000	1,000
Other countries	USGS	–	580	–	–	–
	BGS	–	–	–	–	–
World	USGS	79,000	82,700	77,800	79,000	73,000
	BGS	82,000	86,000	83,000	85,000	86,000

* Country abbreviation according to (ISO, 2014).

** USGS: 2013 (Polyak, 2015); 2014 (Polyak, 2016), 2015 (Polyak, 2017), 2016 (Polyak, 2018), 2017 (Polyak, 2019); BGS: (Brown, 2018).

Table 8
Short summary of reserve classification for minerals according to USGS (Menard, 1976).

Term	Description
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.

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. Man-

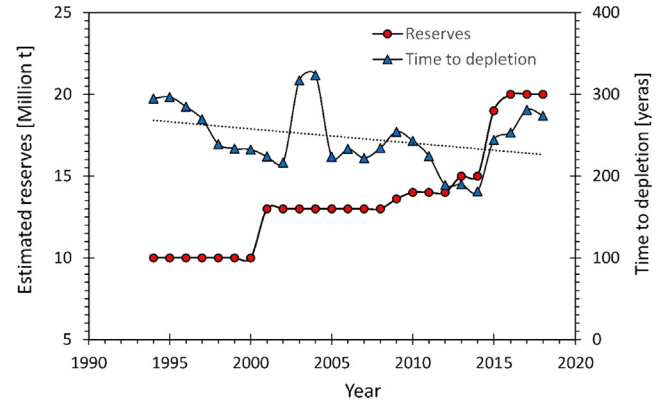


Fig. 5. Reserves of vanadium reported for the period 1994 to 2017 (Hilliard, 1996, 1997; Magyar, 2003, 2004, 2005, 2006, 2007, 2008, 2009; Polyak, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019; Reese, 1998, 1999, 2000, 2001, 2002) and estimation for 2018 (Polyak, 2019) compared to the mine production of the respective year; calculation of time to depletion according to Eq. 2.5.1.

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	No information

ganese is not considered critical but also inadequate for substitution. Even if the prices for Mn (2000 €/t) are much cheaper than

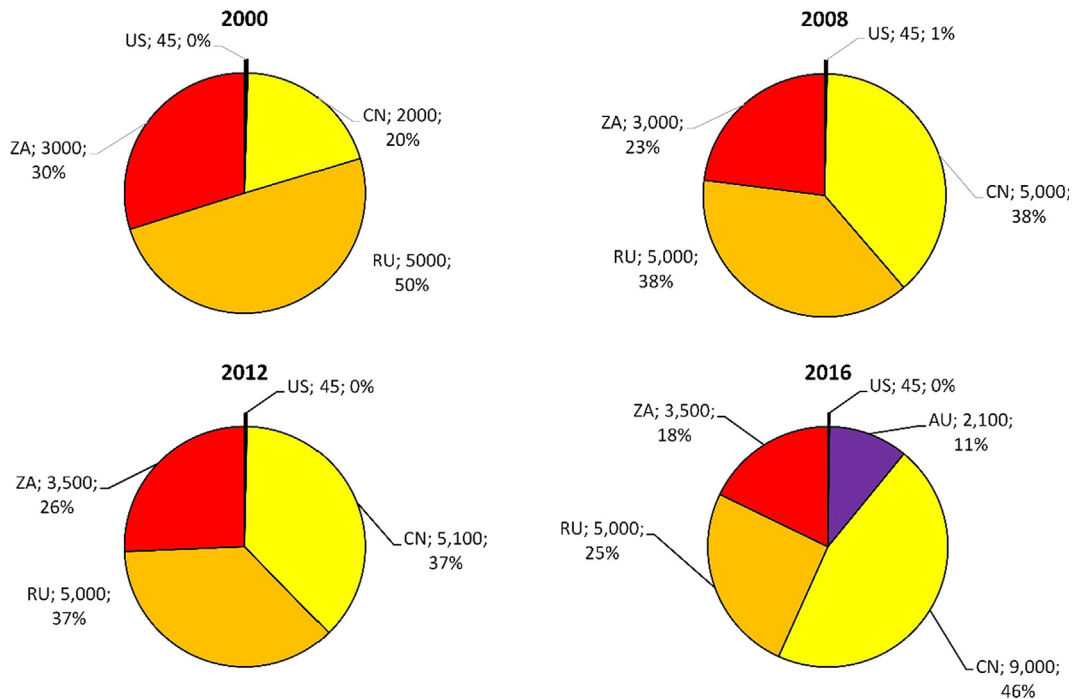


Fig. 4. World mine production of vanadium by country in 1,000 t and share in %; data retrieved from: 2000 (Reese, 2002); 2008 (Polyak, 2010); 2012 (Polyak, 2014); 2016 (Polyak, 2018).

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

Substitute	Critical*	EI*	SR*	Mine production in 2017 [t]	Price [US\$/t]**
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

* (EC, 2017a).

** average price in 2018 according to (Metalary, 2019a, b, c, d, e).

*** average price for ferrovanadium (80%) in 2018 according to (Vanadiumprice.com, 2019).

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 adjustments 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 V_2O_5 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 (V_2O_5) (Vanadiumprice.com, 2019).

4. Properties and applications; future trends

Vanadium is one of the group five elements, and has two naturally occurring isotopes: ^{51}V (stable, 99.75% abundance) and ^{50}V

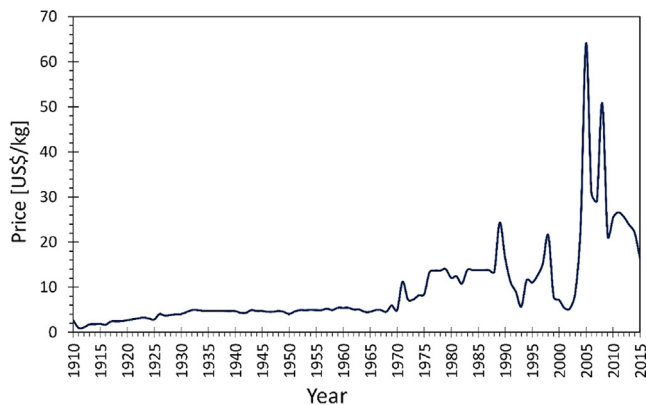


Fig. 6. Price for vanadium pentoxide from 1910 to 2015 in the USA; the price refers to the vanadium content of V_2O_5 , i.e. divided by 0.5602 (Survey, 2016).

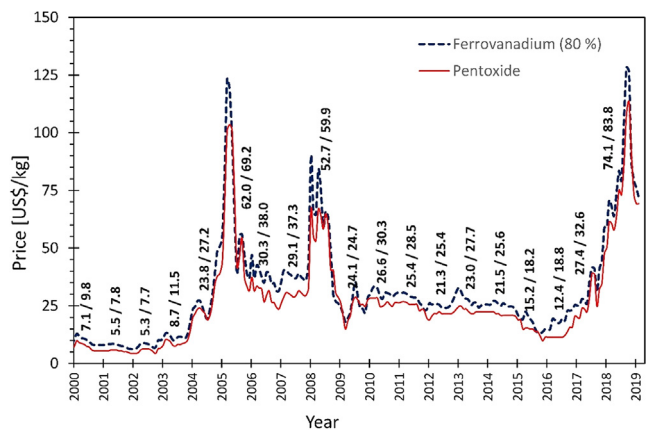


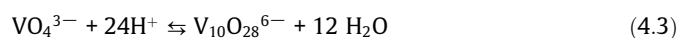
Fig. 7. Price for vanadium pentoxide (refers to the vanadium content of V_2O_5 , i.e. divided by 0.5602) and ferrovanadium (80%) in Europe between January 2000 and March 2019; the numbers indicate the average price over a year (Vanadiumprice.com, 2019).

($t_{1/2} = 1.7 \cdot 10^{17}$ 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 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., V_2O_5). These include the vanadyl ion VO^{2+} , one of the most stable diatomic ions known. High temperatures are required for chemical interactions 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 oxyhalides and pentoxide. Vanadium pentoxide (V_2O_5) is the final product upon heating with excess oxygen but lower oxides can also form, e.g., VO_2 , V_2O_3 or VO . Upon thermal treatment, V_2O_5 loses oxygen reversibly, making it a versatile catalyst. Industrial applications include the oxidation of SO_2 to SO_3 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 V_2O_5 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)).



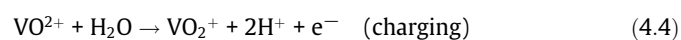
In aqueous solutions, vanadium can form a wide range of oxyanions, depending on pH and concentration. Orthovanadate VO_4^{3-} , which forms at high pH, is important for crystallographic investigations of phosphoryl transfer enzymes (Davies and Hol, 2004), and is a powerful competitive inhibitor of purified 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)).



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 nuclearities have been attained, e.g., $K_{10}[V_{34}O_{82}] \cdot 20H_2O$ (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 VO^{n+} unit in aforementioned polyvanadates resembles Fe^{n+} in biochemical systems. This can provide models for biological systems, e.g., incorporation of VO^{2+} 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 (Moskalyk and Alfantazi, 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 (Moskalyk and Alfantazi, 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 (Moskalyk and Alfantazi, 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). $Li_3V_2(PO_4)_3$ 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, VO^{2+} ions are oxidized to VO_2^+ ions (Eq. (4.4)); at the negative electrode V^{3+} ions are reduced to V^{2+} 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.



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

Table 11
Main applications of vanadium; adapted from (EC, 2011).

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%

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

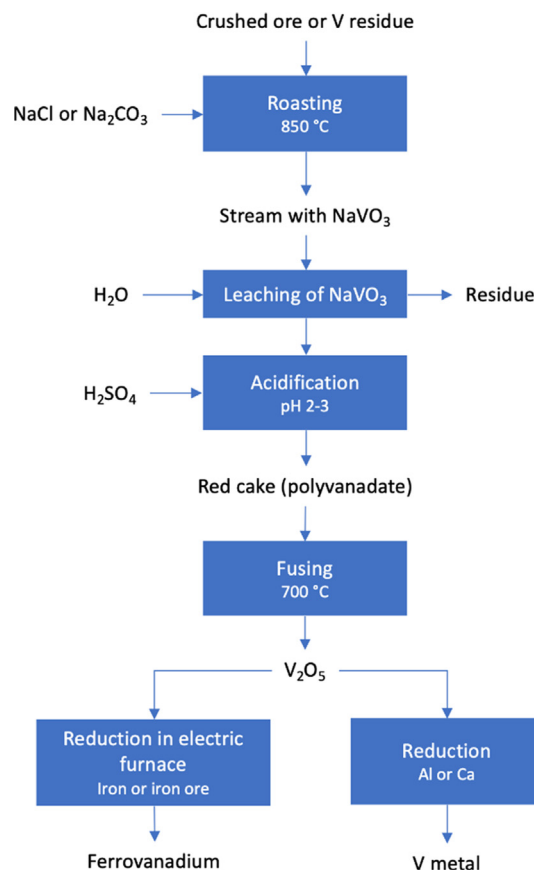


Fig. 8. Typical processing routes to produce vanadium pentoxide and vanadium metal.

Co. Ltd., Hengyang Manganese Product Works, Jinzhou 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 Vanadiy-Tula.

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% V_2O_5 , 2% Al_2O_3 , 1% Fe_2O_3 and 60% SiO_2 ; and the rest constituting several other oxides were in traces/minute quantities (Erust et al., 2016). Another work reported that catalysts contained 27% of V_2O_5 but much larger content of Al_2O_3 (40%) (Villarreal et al., 1999).

Similarly, to catalysts, the increasing demand of steel products leads to the higher volumes of steel making slags generated and it is constantly expanding. Approximately 90% of vanadium is used for steel alloys.

The slag is usually composed of oxides such as: CaO , Fe_2O_3 , SiO_2 and MgO , with smaller amount of Al_2O_3 , MnO , P_2O_5 and TiO_2 . The vanadium ends up in a BOF slag containing approximately 5% of vanadium pentoxide (V_2O_5) (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 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 alloys is higher than niobium, it is well below 4.2% (DIN, 2018).

It can be concluded, that end-of-life steel alloys are the most important source for vanadium recycling as this product group covers 90% of the market. As it makes no sense to recover vanadium from scrap, scrap is re-melted into similar alloys. Recycling of vanadium from steel scrap is thus rather a logistical than a technological issue. However, markets for vanadium other than steel will gain an increasing importance in the future. In particular batteries using vanadium are estimated an emerging technology. In 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 V_2O_5 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,

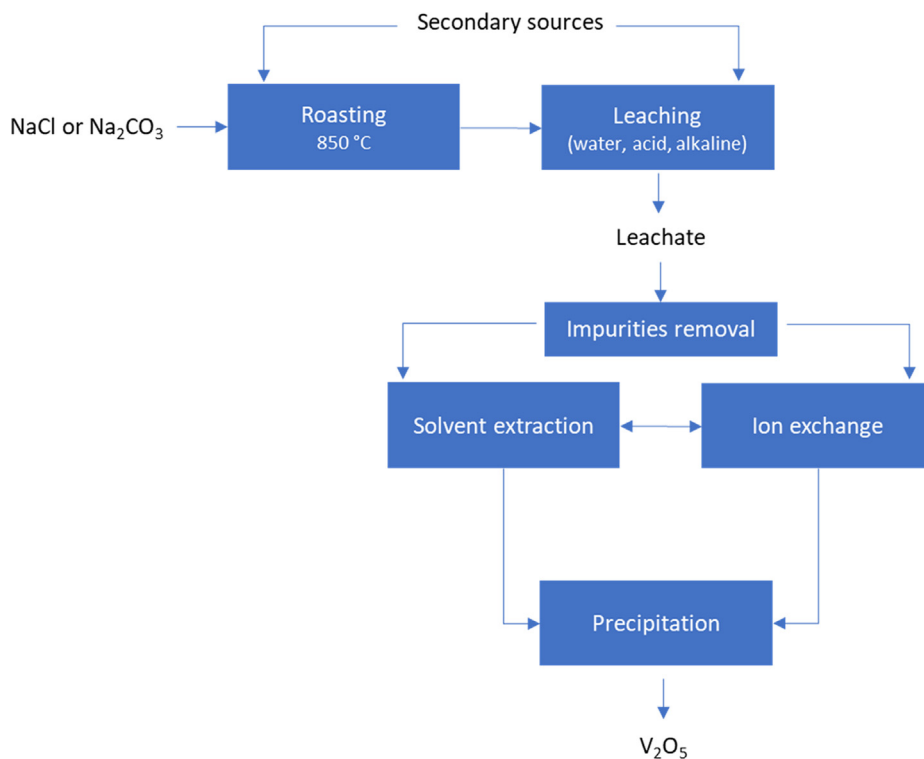
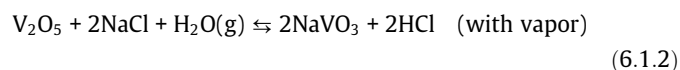
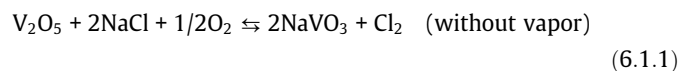


Fig. 9. General flow-sheet of vanadium recycling.

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



In general sodium salts roasting process generates harmful gases, such as Cl_2 , SO_2 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.

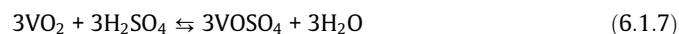
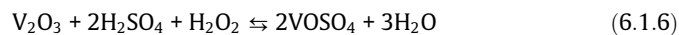
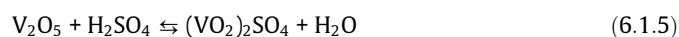
The calcification roasting is considered to be a cleaner alternative to the roasting using sodium carbonate. In the calcination roasting the vanadium slag is processed with limestone or lime. Vanadium is transformed from the vanadium-bearing spinels into calcium vanadates. Vanadium in the vanadium slag is present as FeV_2O_4 spinels which are enraptured by the olive phase Fe_2SiO_3 (Zhang et al., 2012). After the roasting, the olive phase Fe_2SiO_3 is degraded and transformed to CaSiO_3 and Fe_2O_3 . The spinel phase FeV_2O_4 is then subsequently oxidized and transformed to $\text{Ca}_2\text{V}_2\text{O}_7$ and $\text{Ca}(\text{VO}_3)_2$ (Li et al., 2017a). The calcification roasting is environment-friendly due to the elimination of pollutant gas and it is also cost-effective due to the inexpensiveness of lime and limestone. However, during calcification roasting, the phosphorus in vanadium slag is transformed to calcium triphosphate which can react with sulfuric acid and dissolve into the leach liquor of vanadium (Gao et al., 2017a; Li et al., 2016a; Li et al., 2017a).



Innovative NaOH -added pellet was applied to replace traditional Na_2CO_3 - Na_2SO_4 - 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. Valent 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 VO_2^+ . In the alkaline region at pH above 13, VO_4^{3-} 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 VO^{2+} or VO_2^+ ions. In the neutralization step, the VO^{2+} and VO_2^+ 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:



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 H_2O_2 . 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 V^{4+} to V^{5+} 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 $\text{Ba}_3(\text{VO}_4)_2$ is weakly soluble in aqueous solutions (Zeng and Yong Cheng, 2009). Short kinetics and use of stoichiometric amounts of $\text{Ba}(\text{OH})_2$ 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 Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and/or NH_4Cl per ton of V_2O_5 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

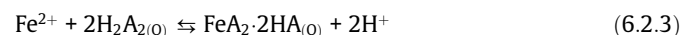
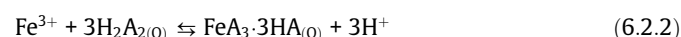
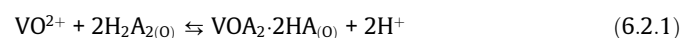
For vanadium recovery by solvent extraction several extractants were used. Among these D2EHPA (Di(2ethylhexyl)phosphoric acid) was used in pilot operations. D2EHPA extracts V^{4+} more strongly than V^{5+} and extraction coefficients of V^{4+} are high enough to be

Table 12

Some of the studies dealing with recovery of vanadium from different sources applying roasting and/or leaching.

Source	Roasting	Leaching reagents	Precipitation/Oxidation agent	Remarks	Metals	Reference
Slag	CaCO ₃	H ₂ SO ₄	–	The calcium sulphate precipitation cover layer significantly affected the internal diffusion of the sulfuric acid into the particles.	V	Xiang et al., 2018
Slag	Calcification	H ₂ SO ₄	–	The leaching process was controlled mainly by the diffusion of solution through surface layer.	V	Peng et al., 2018
Slag	CaO	H ₂ SO ₄	–	Leaching rate of leaching process in the short time range was controlled by solid product layer diffusion. In long time, it was controlled by solid product layer diffusion and chemical reaction.	V	Yang et al., 2014b
Slag	(NH ₄) ₂ SO ₄	H ₂ SO ₄	–	Spinel phases in the vanadium slag, such as FeV ₂ O ₄ , Fe ₂ TiO ₃ , and Fe ₂ MnO ₄ transforms into (NH ₄) ₃ V(SO ₄) ₃ , (NH ₄) ₃ Fe(SO ₄) ₃ , (NH ₄) ₂ Mn(SO ₄) ₂ , and TiSO ₄ at 320 °C and a nearly complete conversion could be achieved at 370 °C.	V, Fe, Ti	Zhang et al., 2018a
Slag	–	H ₂ SO ₄	–	Rate of the leaching is controlled by chemical reaction at low temperature whereas it is controlled by diffusion through the solid product in a long time.	V	Mirazimi et al., 2015
Slag	NaOH-NaNO ₃ (microwave)	Water	–	Leaching time and sample size played a significant role, while leaching temperature and liquid-to-solid ratio showed no obvious effect.	V	Teng and Xue, 2019
Slag	–	NaOH	–	The extraction of vanadium and chromium were both governed by the internal diffusion control using low pressure leaching.	V, Cr	Wu et al., 2018
Slag	Yes	NaOH	H ₂ O ₂ , KClO ₃	The leaching efficiency increased to 85% using 30% KClO ₃ and NaOH.	V, Cr	Yang et al., 2010
Fly ash	–	H ₂ SO ₄	–	The most effective parameter on the recovery of both elements was found to be temperature and the least effective was time for V.	V, Ni	Nazari et al., 2014
Fly ash	burning (850 °C)	H ₂ SO ₄	NaClO ₃	The temperature of the burning step was a significant parameter. Above 950 °C various phenomena (fusion, volatilisation of V, formation of V–Ni refractory compounds) occurred that adversely affected the recovery of vanadium.	V, Ni	Vitolo et al., 2001
Spent catalysts	–	NaNO ₃	–	Optimal conditions were: 0.05 N sodium nitrate (NaNO ₃), pH 8.00, at 25 °C and 1:15 S/L ratio	V	Lai and Liu, 1997
Spent H ₂ SO ₄ catalyst	–	H ₂ SO ₄	–	Optimal conditions were set to: 15% H ₂ SO ₄ ; 1 h; 100 °C; 1/5 S/L ratio) + Oxidative precipitation (73% efficiency)	V	Khorfan et al., 2001
Spent H ₂ SO ₄ catalyst	400 °C	H ₂ SO ₄ and NaOH	–	Optimal conditions for the leaching step were: (0.3 M H ₂ SO ₄) in 6 h at 80 °C and 1:10 S/L ratio.	V	Ognyanova et al., 2009
Spent vanadium catalysts	–	C ₂ H ₂ O ₄	–	Approximately 90% V and 90% K in the catalyst can be leached using oxalic acid.	V, Fe, K	Mazurek, 2013
Vanadium cake (Bayer process)	–	H ₂ SO ₄	–	Optimal conditions were set to: 2 M H ₂ SO ₄ and 40 g/L Na ₂ SO ₃ at 40% pulp density, 70 °C for 1 h	V	Okudan et al., 2015
Selective catalytic reduction (SCR) catalysts	–	NaOH	–	The recovery of vanadium and tungsten from used SCR catalysts leached by 5 M NaOH solution can be achieved with S:L ratio 1:5 at 393 K for 3 h (continuous air stirring, 10 mL/min, 0.05 MPa).	V, W, Ti	Huo et al., 2015

useful in a practical process. The pH-extraction isotherms exhibit that the extraction order would be Fe³⁺ > VO²⁺ > 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):



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 remaining V⁵⁺. During leaching, the RedOx potential was controlled by SO₂

addition to keep vanadium in its V⁴⁺ form. The extraction of vanadium was achieved with a mixture of DEHPA and TBP diluted in kerosene. Vanadium was stripped from the organic solution with 1.5 M sulfuric acid. The concentration of vanadium in the stripping products was approximately 50 g/L. Ammonium polyvanadate (APV) was precipitated by the oxidation and addition of ammonia. The plant was however closed in 1985.

In the more recent research, the mixture of D2EHPA and TPB was still applied in many processes of vanadium recovery (Li 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 (2ethylhexyl)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 Fe³⁺ but not Fe²⁺ and V⁴⁺ is extracted more strongly than V⁵⁺. Sodium sulphide, sodium hydrosulphide or sodium sulphate can be used as reduction agents to reduce Fe³⁺ to Fe²⁺ and V⁵⁺ to V⁴⁺. 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 V⁴⁺ and the comparison study (Li et al., 2012) showed that D2EHPA is a stronger extractant than Cyanex 272. Cyanex 272 also extracts Fe³⁺ and there is a lack of the information about

extraction characteristic related to V^{5+} . On the other hand, Cyanex 301 can extract V^{4+} 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^{4+} (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 ($SF_V = 440$). 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+} (Tavakoli and Dreisinger, 2014). Cyanex 923 showed the best selectivity for V^{5+} over Fe^{3+} by extracting of $VO_2SO_4^-$ 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 H 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. In 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^{4+} had a better extraction ratio than that of V^{5+} , while Fe^{3+} had a serious effect on the extraction of V^{4+} . 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^{4+} was extracted from the real leach solution after reduction process, leaving most of Fe^{2+} , Al^{3+} and Mg^{2+} in the raffinate. Both solvent extraction and ion exchange can be applied in

Table 13

Some of the studies dealing with recovery of vanadium from different leaching media using solvent extraction.

System tested	Remarks	Metals	pH	Reference
D2EHPA	Calculated standard molar enthalpy of the reaction indicated the endothermicity of extraction reaction between VO_2^+ and D2EHPA.	V^{5+}	–	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 $(RNH_2)_4/3(H_3VO_4)$, $(RNH_2)_2(H_3V_3O_9)$ and $(RNH_2)_3(H_6V_{10}O_{28})$.	V^{5+}	–	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^{4+} , V^{5+} , Fe^{3+} , Al^{3+}	2	Shi et al., 2017a
D2EHPA + EHEHPA	The mixture system in the presence of <u>complexing agents</u> exhibit a higher extraction efficiency and require a lower acid consumption during the stripping process of vanadium.	V^{4+}	1.6	Zhang et al., 2016a
D2EHPA + TBP	TBP has no synergistic effect on the VO_2^+ extraction except in the experiments conducted at 60°	V^{5+}	1.8	Cheraghi et al., 2015
D2EHPA (from HCl)	V^{4+} can be separated from other metal ions such as Mg^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} , Al^{3+} and Cu^{2+} in HCl.	V^{4+} , Fe^{3+}	1	Hu et al., 2014
Mextral 973H	The extraction of V^{5+} is strongly dependent on solution pH, and the separation coefficient ($\beta(V/Fe)$) between V^{5+} and Fe^{3+} can be greater than 720 when the solution pH < 0.5.	V^{5+} , Fe^{3+}	0.5	Zhang et al., 2018b
Trialkylamine-N235 + TBP	Vanadium was successfully extracted by a three-stage counter-current process using 20% N235 and 5% tri-butyl phosphate at an organic-to-aqueous (A/O) phase ratio of 2:1.	Fe, Al, Mg, K, Ca, P, Si	1.6	Yang et al., 2016
2-ethyl-1-hexanol	2-ethyl-1-hexanol is found to be a selective extractant for the separation of V^{5+} over Fe^{3+} , U^{6+} , Si^{4+} , and Al^{3+} .	V^{5+} , Fe^{3+} , U^{6+} , Si^{4+} , Al^{3+}	2.0	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., 2014
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 ferric ion reduced into ferrous ion before extracting vanadium. Sodium sulfite was used as the reductant. The reduction rate of ferric ion could reach 98.2%	V^{4+} , V^{5+} , Fe^{3+}	–	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 $VOR_2(HR)_2$ in the high acidity and VOR_2 in low acidity.	V^{4+}	–	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^{4+} , Mo^{4+} , Al^{3+} , Fe^{3+}	1.51	Zeng and Yong Cheng, 2009
Cyanex 301	By using Cyanex 301 as extractant, V^{4+} can be separated from Cu^{2+} and Zn^{2+} (after few stages)	V^{4+} , Cu^{2+}	>1	Karmakar and Biswas, 2019
Cyanex 923	The species extracted into the organic phase was VO_2HSO_4 with one molecule of Cyanex 923	V^{5+}	1–2	Wang et al., 2009
LIX 63	Complete recovery of Mo^{4+} and V^{4+} from Al^{3+} , Fe^{3+} , Co^{2+} and Ni^{2+} can be achieved at pH 1.2–1.5.	Mo^{4+} , V^{4+} , Al^{3+} , Co^{2+} , Ni^{2+} , Fe^{3+}	1.2–1.5	Zhang et al., 1996
LIX 63	The separation factor excellent separation of V^{5+} from Fe^{3+} .	V^{5+} , Fe^{3+}	1.2–1.5	Zeng and Cheng, 2010
Primene 81R, Alamine 336	The extracted species for vanadium at pH 4.5 is $(H_{2-x}V_{10}O_{28})^{x-6}$ with x = 0, 1, 2, and at pH 8 are several vanadates: $(V_4O_{12})^{4-}$, $(V_2O_7)^{4-}$ and $(VO_4)^{3-}$.	V^{5+}	8	Lozano et al., 2003

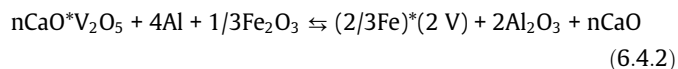
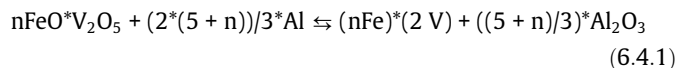
vanadium recovery. D2EHPA has been already applied for vanadium recovery in the industrial applications and seems to be promising extractant since it allows to extract V^{4+} and V^{5+} . However, D2EHPA extracts Fe^{3+} and it can cause the difficulties in vanadium recovery and use of reduction agent 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_4Cl 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 sulfuric media strong anion exchange resin DOWEX 21 K (Zipperian 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 $HClO_4$. 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 (Zhao 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):



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 residue (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 and 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, Nikoloski, 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).

Table 15
Pyrometallurgical processing to improve vanadium recovery.

Approach	Main products	Reference
Aluminothermic reduction of vanadium sludge	Ferrovandium	Suri et al., 1983
Electro-aluminothermic processing	Vanadium droplets and vanadium oxides	Bellemans et al. 2018
CO ₂ addition to oxygen and bubbling into melt	Vanadium	Ray et al. 2013
Furnaces with open slag bath configuration (Evraz Highveld Steel & Vanadium process)	Vanadium oxide and ferrovandium	Steinberg, Geyser, and Nell 2011
Pyrometallurgical processing of vanadiferous slag using silicothermic reduction and byaluminothermic reduction and plasma induction heating	Ferrovandium	Richards et al. 1992

Table 14
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 $VO_2(OH)_2^-$	V^{4+}	4	Zipperian and Raghavan, 1985
DOWEX 50-W	EDTA was used to form stable iron Fe^{3+} EDTA complexes to remove iron from the resin and to increase final purity of vanadium.	V^{4+} , Fe^{3+}	-	Gupta and Krishnamurthy, 1992
D314	Loading of vanadium on the resin can reach 280 mg/mL with overall recovery 98.6% V	V^{5+}	4	Zeng et al., 2009
D314	V was absorbed in the forms of $V_{10}O_{28}$ and $HV_{10}O_{28}$. The maximum distribution ratio of V with the resin was 1475 at pH 4.30 and 35 °C.	V^{5+}	3.2	Zeng et al., 2010
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^{5+} , Mo^{4+}	7.4	Li et al., 2009
Dowex50W-X8	V was separated from Co^{+2} , Mn^{+2} , Ni^{+2} , Zn^{+2} and other metals.	V^{4+} , V^{5+} , Co^{+2} , Fe^{+3} , Mn^{+2} , Ni^{+2} , Ti^{+4} , Zn^{+2}	-	Fritz and Abbink, 1962

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 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.

8. Discussion

The discussion in the present review highlighted how the increasing criticality of vanadium has pushed towards the utilization of secondary sources to replace the traditional mining activities. The study of different kinds of sources (the scientific literature combined with available patents and European funded projects) has proved a particular attention to the development of more sustainable technologies with lower environmental impact and generation of the harmful by-products. Current research activities, summarized in this review, show that it is possible to design the alternatives to traditional methods with better efficiencies and lower footprint, in agreement to the circular economy principles. In this regard, the combination of hydromet-

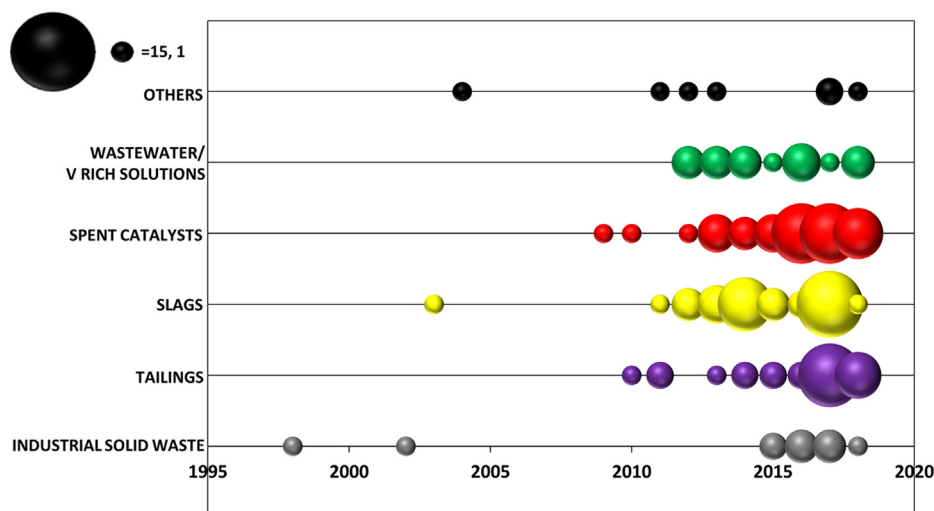


Fig. 10. Technological evolution of the processes for the vanadium recovery. The ball size is proportional to the available number of patents.

Table 16
European Commission funded projects dealing with vanadium recovery.

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 TiO ₂ production process	1983–1985	United Kingdom	TiO ₂ 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

Table 17
Patents dealing with vanadium recovery.

Patent number	Patent title	Year	Reference
US2018297856	Vanadium recovery method	2018	Jung Myungwon, 2018
US2018280941	Method for recycling denitration catalyst (Monsanto Chemicals, 1964; Robinson and Bentley, 2002)	2018	Kiyonaga et al., 2018
CN108160310	Comprehensive recycling method for vanadium-contained coal-pyrite	2018	Du et al., 2018
CN108165741	Method for leaching metal in vanadium titanite-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 titanite-magnetite	2018	Zhang, 2018
CN107970910	Method for recycling waste vanadium catalyst	2018	Xie et al., 2018
CN107904403	Method for comprehensively recycling vanadium-titanium series denitration spent catalyst	2018	Gao et al., 2018
CN107892317	Method for recovering vanadium from calcified vanadium precipitation tailings and preparing nano calcium carbonate	2018	Zhao et al., 2016a
CN107794326	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
CN107699695	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 denitrification catalyst	2018	Chen et al., 2018b
CN107572586	Method for recycling V<2>O<5> 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	Yuan et al., 2017
CN206721309	System for vanadium tailings and copper ashes are carried in processing	2017	Song et al., 2017a
CN107416902	Method of recycling component substances of waste SCR denitration catalyst at low cost	2017	Wang, 2017a
CN107416904	Method of recycling component substances in a waste SCR denitration catalyst	2017	Wang, 2017b
CN107312936	Method for recycling vanadium element from Panzhihua City vanadium titanite-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
CN106957962	Method and system for treating vanadium extraction tailings	2017	Song et al., 2017b
CN106957963	Method and system for treating vanadium extraction tailings	2017	Song et al., 2017c
CN106947864	System for recovering heavy metal from waste SCR catalysts and treatment method thereof	2017	Ning et al., 2017
CN107012276	Comprehensive utilization method for vanadium-titanium magnetite	2017	Deng et al., 2017
CN107012331	Method for recycling vanadium from waste catalyst 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 vanadium 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., 2017e
CN106978542	System and method for processing vanadium and chromium slag of converter	2017	Song et al., 2017f
CN106978541	System and method for processing vanadium and chromium slag of converter	2017	Song et al., 2017g
CN106967885	Vanadium extraction tailing treatment method and system	2017	Wu et al., 2017c
CN106893877	Method for extracting vanadium and chromium from vanadium chromate mixed solution	2017	Wang et al., 2017a

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Table 17 (continued)

Patent number	Patent title	Year	Reference
CN106884090	Sub-molten salt method for totally recycling vanadium, tungsten and titanium from waste denitration catalyst	2017	Wu et al., 2017c
CN106868311	System and method for handling revolving furnace vanadium-chromium slag	2017	Song et al., 2017h
CN106868312	System and method for handling revolving furnace vanadium-chromium slag	2017	Song et al., 2017i
CN106799391	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
CN106636506	Blast furnace smelting method of vanadium titanite-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
CN105986123	Method for extracting vanadium from vanadium-containing waste catalyst reductive organic acid	2016	Li et al., 2016a
CN105950873	Method for recycling vanadium, tungsten and titanium from waste SCR denitration catalyst	2016	Liu et al., 2016
CN105905945	Recycling treatment method for wasted SCR catalyst	2016	Zhao and Ming, 2016
CN105861829	Method for separating vanadium and chromium solution and recycling vanadium and chromium	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
CN105753219	Process for purifying and treating vanadium-containing wastewater in advanced manner and process for recycling vanadium and chromium	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
CN105567964	Method for selectively reducing, separating and recycling vanadium and chrome from solution containing vanadium and chrome	2016	Wang et al., 2016a
CN105420519	Method for extracting vanadium and chromium from materials containing vanadium or/and chromium	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 of silicate vanadium ores	2016	Li et al., 2016
CN105296762	Method for preparing vanadium liquid through vanadium oxide industrial waste water	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) equilibrium catalyst	2016	Guo and Liu, 2016
CN105217685	Method and apparatus for recycling vanadium pentoxide from waste flue gas denitration catalyst	2016	Su et al., 2016
CN105112690	Method for recycling vanadium and silicon simultaneously from silicious type vanadium ore	2015	Xing et al., 2015
CN105112678	Method for magnetically separating and smelting chromium-iron alloy by vanadium extraction from vanadium-chromium slag and reduction of tailings	2015	Li et al., 2015a
CN105087961	Method for efficiently recycling vanadium, iron and titanium in vanadium-titanium metallized pellet through electric arc furnace	2015	Hongzhi, 2015
CN105087933	Method for separating vanadium and chromium from vanadium and chromium mixed solution	2015	Li et al., 2015b
CN104928464	Method for extracting valuable metal in vanadium containing material by microwave heating preprocessing	2015	Zhang et al., 2015a
CN104831075	Method for separating and purifying vanadium and molybdenum of waste vanadium-molybdenum SCR (selective catalytic reduction) catalyst	2015	Lin et al., 2015
CN104726715	Recycling method for vanadium-chromium waste residues	2015	Li et al., 2015c
CN104649328	Method of preparing ferric vanadate from residue of aluminum powder vanadium removal of crude titanium tetrachloride	2015	Zhang et al., 2015b
CN104611564	Method for recycling metal oxides from waste SCR (selective catalytic reduction) catalyst	2015	Li et al., 2015a
CN104495873	Method for extracting vanadium and tungsten metals from waste SCR honeycomb catalyst	2015	Wang et al., 2015b
TW201516156	Method for recycling vanadium and tungsten from waste selective catalytic reduction catalyst	2015	Chen et al., 2015
CN104388683	Method for separating and recycling vanadium and chromium from vanadium and chromium-containing material	2015	Wang et al., 2015b
CN104195342	Method for recycling vanadium pentoxide in waste SCR (Selective Catalytic Reduction) denitration catalyst	2014	Lu et al., 2014a
CN104178638	Method for separating and recycling vanadium and chromium from chromium vanadium reducing slag	2014	Wu et al., 2014a
CN104178637	Method for separating and recycling vanadium and chrome from vanadium-chrome slag	2014	Wu et al., 2014b
CN104152698	Recycling method of vanadium-nitrogen alloy waste materials	2014	Guangkai, 2014
CN104099476	Recycling method for waste denitration catalyst	2014	Lin et al., 2014
CN104086032	Method for recycling vanadium precipitating wastewater	2014	Chen et al., 2014
CN104046786	Method for recovering metals from vanadium slag	2014	Zhaoqian, 2014
CN104017999	Vanadium extraction method for converter vanadium slag	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, aluminum, scandium, titanium, vanadium and the like in red mud	2014	Dong et al., 2014
CN103898329	Method for extracting vanadium from vanadium slag through manganese roasting	2014	Yin et al., 2014

Table 17 (continued)

Patent number	Patent title	Year	Reference
CN103849774	Method for recycling waste SCR (Selective Catalytic Reduction) catalyst	2014	Lu et al., 2014b
CN103849765	Method for precipitation separation and recovery of chromium and vanadium in chromium-vanadium solution	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 vanadium, chromium, phosphorus and calcium	2014	Liu et al., 2014
CN103526019	Method for comprehensive recycle of vanadium, selenium and silver from multi-metal associated vanadium ore	2014	Jiang et al., 2014
CN103409633	A method of recycling vanadium from removed silicon slag	2013	Yin et al., 2013a
CN103343174	Method for separating titanium, iron, vanadium and calcium from mixed titaniferous slag	2013	Zhang et al., 2013b
CN103276218	Method for recycling vanadium from vanadium-containing electrolysis aluminum slag ash	2013	Zhou et al., 2013
TW201323622	Method for recycling metal oxide from denitrification waste catalyst	2013	Sun et al., 2013a
TW201315815	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 waste slag by superconduction high-gradient magnetic separation technology	2013	Li et al., 2013b
CN103045868	Method for extracting vanadium from extracted vanadium tailings	2013	Zhang et al., 2013a
CN102936039	Recovery process of honeycomb type selective catalytic reduction (SCR) waste catalyst containing tungsten, vanadium and titanium	2013	Rui, 2013
CN102925693	A method for extracting metal in waste catalyst RDS / HDS by using acid leaching	2013	Yulong et al., 2013
CN102899487	Process for leaching vanadium out of stone coal by using oxidant and sulfuric acid	2013	Yan et al., 2013
CN102876899	Method for effectively separating and extracting vanadium and chromium from vanadium-leaching wastewater	2013	Li et al., 2013c
CN102876895	Method for recycling vanadium and chromium from low-concentration pentavalent vanadium and hexavalent chromium mixed liquor	2013	Yin et al., 2013a
CN102864318	Method for recycling vanadium from acid vanadium-containing solution containing silicon and phosphorus	2013	Xing et al., 2013
CN102732736	Method for extracting vanadium from burning slag of stone coal vanadium mine fluidized bed	2012	Ailiang and Jinqiang, 2012
CN102676810	Method for separating and recycling vanadium and chromium from vanadate-chromate-containing solution	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 slag	2012	Lanjie and Ruiguo, 2012
CN102491419	Method for comprehensively recycling waste vanadium catalyst	2012	Shaoming and Bin, 2012
CN102345020	Method for separating and recycling vanadium and chromium in solution	2012	Zibi et al., 2012a
CN102337411	Method for recycling vanadium and chromium from high-chromium low-vanadium vanadium precipitation wastewater	2012	Zibi et al., 2012b
CN102337410	Method for recycling vanadium from dephosphorization base flow residues	2012	Zibi et al., 2012c
CN102251119	Method for recycling vanadium extraction tailings	2011	Hao et al., 2011
CN102061397	Method for recycling vanadium, chromium, titanium and iron from vanadium-titanium magnetite ore	2011	Housheng et al., 2011
CN102060328	Method for completely recycling vanadium-containing stone coal	2011	Dehong et al., 2011
CN102021345	Method for recycling vanadium pentoxide and sodium dichromate	2011	Denglun et al., 2011
CN101921916	Method for recycling metal oxide from waste flue gas denitration 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
KR20090108981	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

allurgical and pyrometallurgical approaches can lead to increase the material recovery rates since hydrometallurgy allows for more selective metal separation and provides the ability to re-utilize chemical reagents or by-products within the production. Therefore, future perspectives include the sustainability increase of the recovery processes, also combining established techniques with innovative approaches.

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