FUTURE BATTERY INDUSTRIES CRC

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ABSTRACT

The commercialisation of vanadium redox flow batteries for large scale electric energy storage and power grid stabilisation is expected to increase the global demand for vanadium in the coming years. Currently most of the vanadium is used in the production of steel alloys and this amount is expected to remain consistent in the years to come. Much of the new demand is expected to come in the form of electrolytes for the application of vanadium to energy storage in the vanadium redox flow batteries and in the form of ultrapure vanadium salts for use a precursor reagents in the production of cathodes for lithium ion batteries.

Unlike other metals such as copper, nickel or zinc, vanadium does not form concentrated deposits. Owing to the similarities between the V^{3+} and Fe^{3+} cations, vanadium is often found as a minor component of iron minerals. The vanadium mineral coulsonite, FeV_2O_4 forms series with chromite, $FeCr_2O_4$ and magnetite, Fe_3O_4. Most of the vanadium is produced from titanomagnetites either directly from titanomagnetite ores/concentrates or indirectly from the slag left from smelting titanomagnetite ores. Titanomagnetite ores are associated with mafic igneous rock and have been found in large quantities in Russia, China, South Africa and other countries. Vanadium can also be produced from vanadiferous sandstone, shale and vanadate deposits, though these are of lesser industrial importance compared to titanomagnetites.

Vanadium is usually extracted from ores, concentrates and slags by roasting with sodium carbonate or another sodium salt to convert vanadium into water soluble sodium vanadates. This document summarises the established and proven technology for vanadium production, specifically focusing on salt roasting as it is one of the most widely applied processing options, as well as some newer processes which have yet to be commercialised.

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1 INTRODUCTION

1.1 Vanadium properties and applications

Vanadium is primarily used as an additive to steel in the form of ferrovanadium (Moskalyk and Alfantazi, 2003). Around 85% of the vanadium produced globally is used for this purpose (Swinbourne et al., 2016). Only minor amounts of vanadium are needed for this purpose, with vanadium comprising just 0.05-0.2% of the mass of the steel in high-strength low-alloy steel (HSLA) widely used in construction and motor vehicles (Kelley et al., 2017).

Vanadium improves the strength of titanium, and vanadium-titanium alloys have been used in the construction of aircraft. Alloys of vanadium, chromium and titanium also have suitable properties for the construction of nuclear reactors. These alloys are durable at high temperature and resistant to corrosion from water as well as the alkali metals sometimes used as a heat exchange medium in nuclear reactors. Vanadium has a low neutron capture cross section and is resistant to radiation damage, making these V/Cr/Ti alloys superior to stainless steel in nuclear applications (Gupta and Krishnamurthy, 1992).

Vanadium compounds are also used as catalysts, and have been used in the chemical industry as early as the 1870s (Gupta and Krishnamurthy, 1992). The oxidation of SO2 to SO3 in the production of sulphuric acid is catalysed by vanadium oxides (Garcia-Labiano et al., 2016).

A more recent application for vanadium is in energy storage. Vanadium is used in the cathodes of some lithium ion batteries. A newer energy storage application is in redox flow batteries, which can charge and discharge simultaneously. Vanadium redox flow batteries (VRBs) have been proposed as a way to stabilise the output from remote stand-alone wind power generation facilities (Barote et al., 2008). A major advantage of vanadium redox flow batteries over other variants such as iron-chromium redox flow batteries is that they use the same element on both sides of the electrolyte separating membrane, eliminating the problem of cross-contamination by osmotic diffusion and/or a permanent reduction in capacity in the event of a leak between the oxidised and reduced sides (Skyllas-Kazacos et al., 2011).

Vanadium redox batteries rely on the stability of various vanadium redox states in aqueous solution. Vanadium cycles between the 4+/5+ states on the cathode side (Reaction 1), and between the 2+/3+ states on the anode side (Reaction 2; Li et al., 2011a).

$$VO^{2+} + Cl^- + H_2O \leftrightarrow VO_2Cl + 2H^+ + e^- \qquad \text{Reaction 1}$$

$$V^{3+} + e^- \leftrightarrow V^{2+} \qquad \text{Reaction 2}$$

The vanadium solutions may be stored in large tanks (Figure 1; Algar, 2017), allowing the battery to be scaled up by simply building bigger tanks. A large vanadium redox battery (200 MW/800 MWh capacity) is under construction on the Dalian Peninsula in China, and is expected to go online in 2020 (UniEnergy Technologies, 2016)

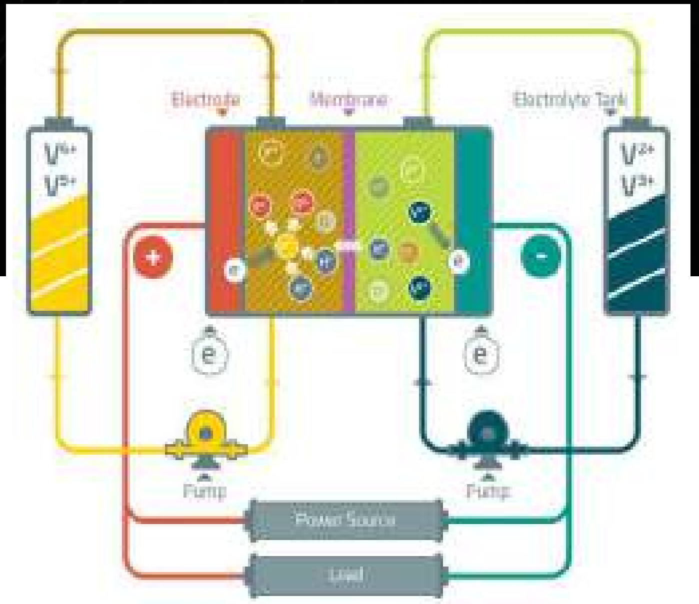


Figure 1. Illustration of a vanadium redox flow battery from Algar (2017).

1.2 Global supply and demand

The price of vanadium has been historically volatile (Anon, 2011; Geoscience Australia, 2014; Polyak, 2016). The majority of vanadium is produced as a co-product from slag, given its high affinity for oxygen and tendency to report in the oxide phase during the smelting for production of steel. Of the remainder, in 2015 approximately 18% was produced from primary vanadium ores and 11% from secondary sources (Figure 2 after Perles, 2016).

As the majority of vanadium is added to steel, the annual demand for vanadium tends to follow the annual demand for steel (Leont'ev and Shavrin, 2000; Raja, 2007). Stricter regulations around the use of high-strength steel have however increased the demand for vanadium as a steel additive (Anon, 2011).

The remainder of vanadium is used in titanium alloys and catalysts with a small amount currently used for energy storage applications (Algar, 2017). The vanadium demand for energy storage applications is expected to grow significantly in the coming years (Figure 2 after Algar, 2017).

The recent closure of the Highveld steelworks in South Africa, a major producer of vanadium from steel slag has led to a decrease in supply. With the anticipated growth in vanadium demand for energy storage applications, new primary vanadium mines will be needed to meet demand (Perles, 2016).

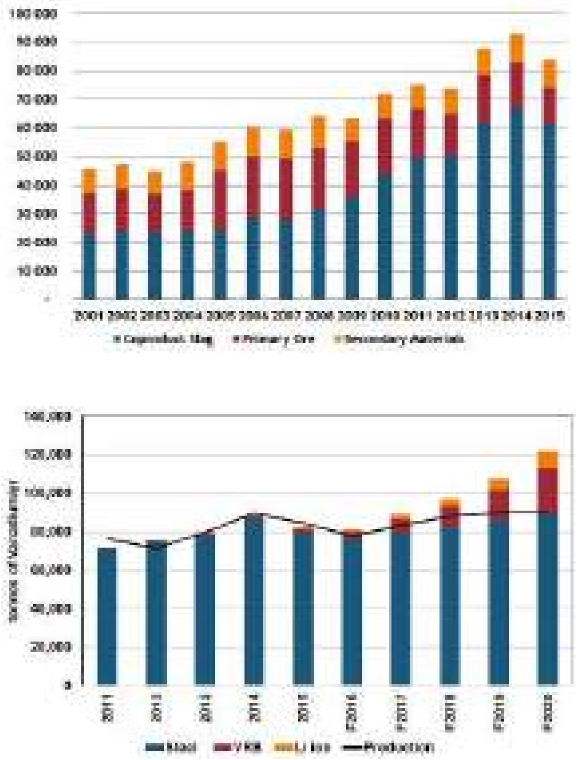


Figure 2. Top: sources of vanadium modified from Perles (2016). Bottom: uses of vanadium modified from Algar (2017).

1.3 Occurrences and sources

1.3.1 Geology and mineralogy of vanadium ores

Vanadium does not form concentrated deposits like other metals such as copper, nickel or zinc. It is widely dispersed in the Earth's crust, with V^{3+} replacing Fe^{3+} or Al^{3+} in a number of minerals. Vanadium as V^{3+} can substitute for Fe^{3+} in magnetite (Wenk and Bulakh, 2004); vanadium(III) and iron(III) ions have near identical ionic radii in octahedral sites of crystal lattices - 64.5 and 64.0 pm respectively (Schwertmann and Pfab, 1996). The mineral coulsonite (FeV2O4) is often associated with magnetite (Radtke, 1962) and forms a series with magnetite and chromite, FeCr2O4 (Reznitsky et al., 2005). Ilmenite is also known to host vanadium (Xu et al., 2017). Hence, iron and titanium deposits are a major source of vanadium (Gupta and Krishnamurthy, 1992; Dill, 2010).

Likewise, much of the vanadium in titanomagnetite ores is associated with magnetite, with ilmenite containing relatively small amounts of the vanadium present in such ores. However the liberation size of titanium mineralisation in these deposits can be as low as 5 μm, with fine laths of titanium minerals included in iron minerals (Taipale, 2013). These laths form as the phases separate during cooling of the original magmatic intrusion. In practical terms, these textures can lead to difficulties in separating ilmenite from magnetite during beneficiation (Connelly et al., 2008).

The majority of vanadium in titanomagnetite deposits occurs as V^{3+}, with a small amount of V^{4+}. X-ray absorption near edge structure spectroscopy (XANES) of seven titanomagnetite samples from different locations has shown that only approximately 2-17% of the vanadium was present as V^4+ (Balan et al., 2006). Vanadium as V4+ can replace Ti^{4+} in ilmenite. The redox conditions in the original melt will affect the ratio of V^{3+} to V^{4+} which will in turn affect how vanadium partitions between magnetite and ilmenite in titanomagnetites (Schuiling and Feenstra, 1980).

Vanadium in weathered mineral deposits is known to occur in clay, with V^{3+} replacing Al^{3+} in phyllosilicates and replacing Fe^{3+} in goethite, FeOOH (Goddard and Fox, 1981; Schwertmann and Pfab, 1996). Chlorite, $(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$, and goethite containing vanadium have been identified in weathered zones of vanadium titanomagnetite deposits (Habteselassie et al., 1996). Additionally, many uranium deposits contain vanadium in the form of uranyl vanadate minerals such as carnotite, $K_2(UO_2)_2V_2O_8.3H_2O$ or tyuyamunite, $Ca(UO_2)_2V_2O_8.5\text{-}8H_2O$ (Lauf, 2016).

Dellagiustaite, a spinel type mineral containing V^{2+} was discovered at Sierra de Comechingones, Argentina in 2017, with the ideal formula of $V^{2+}Al_2O_4$ and an empirical formula of $(V^{2+}{}_{0.91}Mg_{0.08}Mn_{0.01}Al_{1.09}V^{3+}{}_{0.88}Ti^{3+}{}_{0.03})_{\Sigma 3}O_4$. Another occurrence of the same mineral was subsequently discovered in volcanic rock from Mt. Carmel near Haifa, Israel (Cámara et al., 2019). The volcanic rock from Mt. Carmel formed under reducing conditions and therefore natural metallic vanadium and vanadium hydride (VH2) were also present in the rock (Bindi et al, 2019).

1.3.2 Secondary sources of vanadium

Vanadium, as well as titanium, can be recovered from the slags generated in the smelting of titanomagnetite ores (Gabra and Malinski, 1981; Hukkanen and Walden, 1985; Chen et al., 2013) or the refining of steel (Hitching and Kelly, 1982; Steinberg et al., 2011). Large accumulations of such slags can be found in various locations in the world. The majority of world vanadium production comes from slag (Perles, 2016).

Vanadium has been produced as a by-product of uranium mining at several mines in the south-western areas of the USA from ores rich in minerals such as carnotite (Merritt, 1971). Similar deposits have been identified in Western Australia (Liu and Jaireth, 2011). When leaching uranium/vanadium ores, uranium will dissolve more readily than vanadium, with vanadium requiring more aggressive conditions. Some mines in the USA used a mild leach to dissolve most of the uranium, followed by a more intense leach to dissolve vanadium from the uranium leaching residue (Merritt, 1971). A similar approach has been proposed for the processing of shale-hosted uranium/vanadium ore from South Korea (Henning, 2013).

Vanadium also occurs in small amounts in coal (Wang et al., 2015) and bituminous shale (Brooks and Potter, 1974). A large oil shale deposit containing vanadium and minor amounts of molybdenum has been identified near Julia Creek in northern Queensland (Lewis et al., 2010). The Okcheon belt in South Korea hosts several deposits of shale rich in vanadium and uranium (Henning, 2013). While a salt roast process is planned for the Daejon vanadium/uranium shale project in the Okcheon belt in South Korea (Protean Energy, 2019), the alkaline carbonate leaching process for uranium is also effective for vanadium extraction from Korean shale. Maximum extractions of 90% for U and 65% for V have been reported (Kim et al., 2014). The process selected for such ores will depend on whether vanadium or uranium extraction is prioritised.

Of other potentially significant sources, vanadium has also been identified in phosphate rock (Russell et al., 1982; Judd et al., 1986) and traces of vanadium are present in crude oil (Dechaine and Gray, 2010). Venezuelan crude oil in particular is high in vanadium, with up to 0.05 % recorded in some areas (Gupta and Krishnamurthy, 1992). The vanadium in the oil reports to the ash when it is burned (Vitolo et al., 2000; Holloway and Etsell, 2004) and this can lead to the release of toxic vanadium pentoxide dust or fumes into the atmosphere and corrode turbines when used in power generation (Dechaine and Gray, 2010).

2 OVERVIEW OF VANADIUM PRODUCTION TECHNOLOGY

While vanadium production flow sheets vary between different mines and processing plants, there are a few common features. The process used will vary depending on the nature of the ore. Most vanadium is produced from titanomagnetite ores, either directly or from the slag generated by smelting of titanomagnetite ores. For this reason, this review is focused on vanadium production from titanomagnetites.

The flowsheet below shows a typical process for producing vanadium directly from titanomagnetite ore and is based on the processes used at Windimurra in Australia (Swinbourne et al., 2016), Otanmäki in Finland (Hukkanen and Walden, 1985), the Menchen mine in Brazil (Largo Resources, 2016) and the Vantra roast-leach plant in South Africa (Rohrmann, 1985).

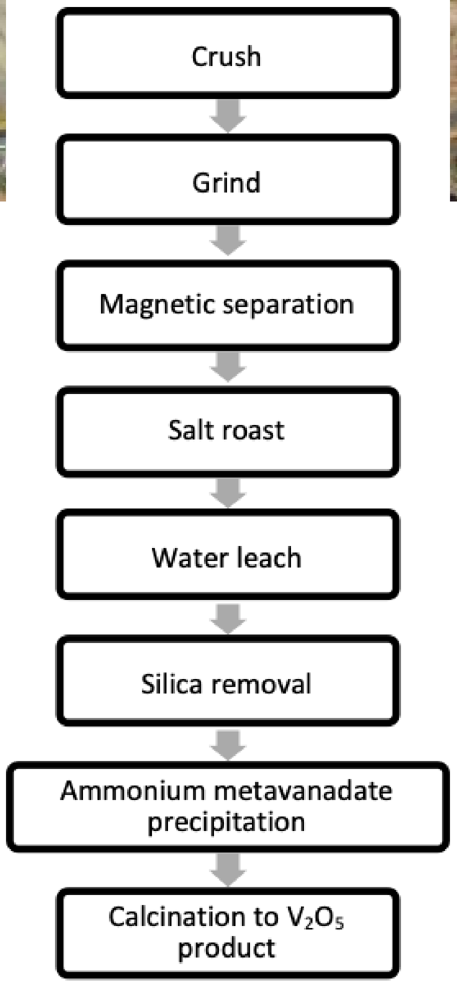


Figure 3. Generic vanadium production flowsheet from titanomagnetites, based on several industrial examples.

2.1 Salt roasting

Salt roasting can be applied to whole ore, to a concentrate or to slags produced by other smelting processes. The current knowledge of this unit operation that is available in the public domain literature is summarised below.

2.1.1 Treatment of ores and concentrates

Magnetic beneficiation is effective for producing a vanadium enriched concentrate from vanadium bearing titanomagnetite ores (Gabra and Malinsky, 1981). A salt, usually sodium carbonate or sodium chloride is added to the vanadium ore/concentrate and heated to 800-1000°C to convert the contained vanadium into water soluble sodium vanadate compounds (Gupta and Krishnamurthy, 1992). Sodium sulphate, oxalate and hydroxide salts are also effective and are discussed later in this review.

Vanadium pentoxide reacts with the sodium carbonate forming sodium metavanadate by the following reaction:

$V_2O_5 + Na_2CO_3 \rightarrow 2\ NaVO_3 + CO_2$ **Reaction 3**

Salt roasting under oxidising conditions will oxidise V3+/V4+ minerals to V5+ compounds (van Vuuren and Stander, 2001). This increases the solubility of vanadium. Magnetite is oxidised to hematite in the initial stage of the process and vanadium diffuses out of the lattice, where it is able to react with the added sodium salts and oxygen, forming sodium vanadates (Hukkanen and Walden, 1985).

$V_2O_3 + Na_2CO_3 + O_2 \rightarrow 2\ NaVO_3 + CO_2$ **Reaction 4**

$FeV_2O_4 + Na_2CO_3 + 1.25\ O_2 \rightarrow 2\ NaVO_3 + 0.5\ Fe_2O_3 + CO_2$ **Reaction 5**

$VO_2 + 0.5\ Na_2CO_3 + 0.25\ O_2 \rightarrow NaVO_3 + 0.5\ CO_2$ **Reaction 6**

Adding an excess of sodium to the roasting process may form sodium pyrovanadate ($Na_4V_2O_7$) or sodium orthovanadate (Na_3VO_4) (Gupta and Krishnamurthy, 1992).

$V_2O_3 + 2\ Na_2CO_3 + O_2 \rightarrow Na_4V_2O_7 + 2\ CO_2$ **Reaction 7**

$V_2O_3 + 3\ Na_2CO_3 + O_2 \rightarrow 2\ Na_3VO_4 + 3\ CO_2$ **Reaction 8**

Sodium pyro- and orthovanadate both melt at higher temperatures than sodium metavanadate however (Figure 4).

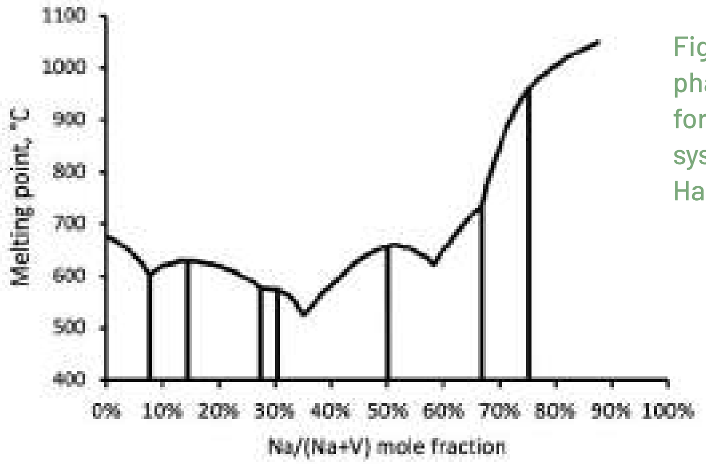


Figure 4. Binary phase diagram for the Na-V oxide system, after Hausen 1984.

Thermochemical modelling with HSC Chemistry v7.1.1 (Roine, 2011) has confirmed that sodium pyrovanadate and orthovanadate are not expected to form until high doses of sodium are added. Other oxides in the ore/concentrate may be converted to soluble sodium compounds as well. In some cases this is desirable, as it can enable the recovery of chromium as a by-product.

$Cr_2O_3 + 2\ Na_2CO_3 + 1.5\ O_2 \rightarrow 2\ Na_2CrO_4 + 2\ CO_2$ **Reaction 9**

$MgCr_2O_4 + 2\ Na_2CO_3 + 1.5\ O_2 \rightarrow 2\ Na_2CrO_4 + MgO + 2\ CO_2$ **Reaction 10**

$FeCr_2O_4 + 2\ Na_2CO_3 + 1.75\ O_2 \rightarrow 2\ Na_2CrO_4 + 0.5\ Fe_2O_3 + 2\ CO_2$ **Reaction 11**

$TiO_2 + Na_2CO_3 \rightarrow Na_2TiO_3 + CO_2$ **Reaction 12**

$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2$ **Reaction 13**

$Al_2O_3 + Na_2CO_3 \rightarrow 2\ NaAlO_2 + CO_2$ **Reaction 14**

After roasting, vanadates dissolve through Reaction 21-Reaction 24 listed in Section 3.3.3 below. The other sodium compounds formed dissolve through Reaction 25-Reaction 30.

2.1.2 Recovery from steel slags

The salt roasting process described above can also be applied to vanadium rich slags. The chemistry of vanadium extraction from vanadium-rich slag by the salt roast/water leach process is quite similar to that involved when processing ores and concentrates, although the optimum conditions and reagent dosages will differ from those for the processing of ores/concentrates. These slags are produced during the refining of iron and steel produced from vanadiferous iron ores. The following section deals with the chemistry involved in the production of slags suitable for salt roasting from pig iron during the steel production process.

2.2 Smelting

Some vanadium will be reduced to the metallic state during the smelting of vanadiferous titanomagnetite ores in electric arc furnaces. Titanomagnetite ores are not suitable for smelting in blast furnaces due to the formation of titanium carbides/nitrides (Reaction 15, after Yan et al., 2013), resulting in viscous sticky slag (Smirnov et al., 2001). Electric furnaces must be used instead (Robiette, 1973; Rosenqvist, 1983).

$$4\,TiO_2 + N_2 + 10\,C \rightarrow 2\,TiC + 2\,TiN + 8\,CO \qquad \text{Reaction 15}$$

Careful control of the carbon addition is necessary to maximise the recovery of vanadium into the pig iron while avoiding the formation of titanium carbides (Robiette, 1973). Iron is more readily reduced than vanadium, chromium or titanium.

In the next stage of refining the iron/steel, it is necessary to remove the vanadium into the slag if the vanadium content of the metal is too high. This slag is suitable feedstock for salt-roasting processes to recover vanadium (Hitching and Kelly, 1982; Rohrmann, 1985; Lindvall and Ye, 2012). Other metals such as chromium may also be produced this way (Li et al., 2015).

The EHSV plant in South Africa and the Glenbrook steel plant in New Zealand have used oxygen sparging processes to draw vanadium from the intermediate pig iron product into a slag suitable for the salt roasting process (Kelly, 1993; Steinberg et al., 2011).

$$2\,V_{(metal)} + 1.5\,O_{2(g)} \rightarrow V_2O_{3(slag)} \qquad \text{Reaction 16}$$

$$Fe_{(metal)} + 0.5\,O_{2(g)} \rightarrow FeO_{(slag)} \qquad \text{Reaction 17}$$

$$2\,V_{(metal)} + 3\,FeO_{(slag)} \leftrightarrow 3\,Fe_{(metal)} + V_2O_{3(slag)} \qquad \text{Reaction 18}$$

Silicon in the metal can also reduce vanadium into the metallic state (Reaction 19), and ferrosilicon may be used to recover vanadium from slag (Lindvall and Ye, 2012). Increased slag basicity lowers the activity of SiO_2 in the slag, favouring the partition of vanadium into the metal (Ressel et al., 2005; Yan et al., 2013).

$$3\,Si_{(metal)} + 2\,V_2O_{3(slag)} \leftrightarrow 4\,V_{(metal)} + 3\,SiO_{2(slag)} \qquad \text{Reaction 19}$$

Lime will also react with titanium dioxide in slag, preventing the formation of titanium carbides/nitrides, lowering slag viscosity and improving vanadium diffusion (Yan et al., 2013).

$$CaO_{(slag)} + TiO_{2(slag)} \rightarrow CaTiO_{3(slag)} \qquad \text{Reaction 20}$$

Once vanadium is in the slag, a higher basicity (i.e. oxide ion activity) will promote the oxidation of vanadium to the pentavalent state. The effect of slag basicity on the vanadium redox state is greater at higher temperature (Figure 5 after Inoue and Suito, 1982).

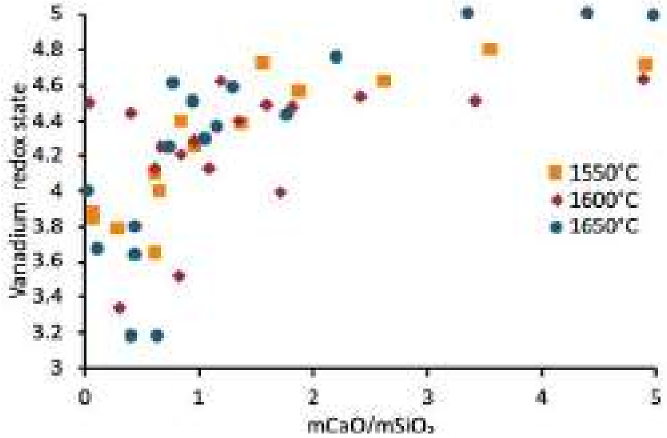


Figure 5. Average redox state of vanadium in slag as a function of the CaO/SiO_2 mass ratio in the temperature range 1550-1650°C. Adapted from a figure by Inoue and Suito (1982).

A similar trend has been identified in the Na_2O/SiO_2 system (Chaudary et al., 1997), although these slags are not stable in contact with carbon saturated iron melts (Gustaffson and Zhong, 1985). A lower p_{O2} value is needed to oxidise V^{3+} to V^{5+} at higher basicity (Chaudary et al., 1997). Vanadium trioxide in the slag may react with ferrous oxide (also in the slag) forming the solid spinel FeV_2O_4, which can be removed from the slag and recovered (Gustaffson and Zhong, 1985).

Considering these reactions and equilibrium states, it seems that high slag basicity is more favourable when smelting ore to produce pig iron, while a low basicity is preferred when recovering vanadium into slag. It is also important to consider downstream impacts however. Slags high in silica (low basicity index) require greater amounts of sodium carbonate in the salt roasting process due to competing reactions. Some magnetic separation may also be necessary to remove metallic iron entrained in slag before salt roasting (Gabra and Malinsky, 1981).

2.3 Leaching

2.3.1 Vanadium solubility and stable species

The aqueous chemistry of vanadium is complicated, with redox states 2 through 5 being stable. Pentavalent vanadium is stable over a large range of pH values, and is the only form stable in the presence of air (Gupta and Krishnamurthy, 1992; Figure 6).

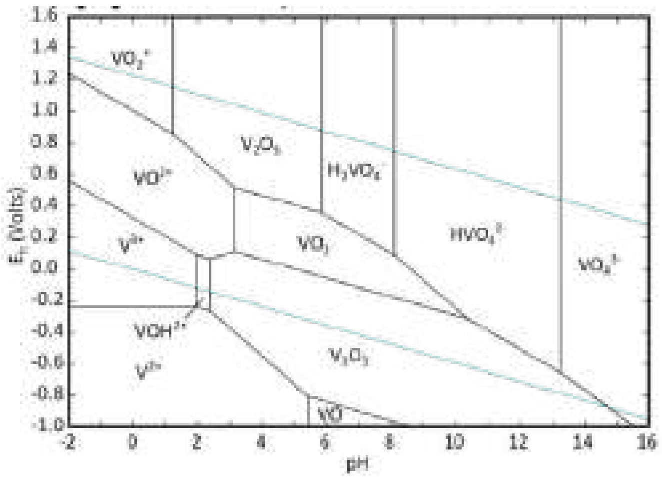


Figure 6. Pourbaix diagram showing the distribution of vanadium species in a 0.01 mol/L vanadium solution at 25°C, produced in HSC Chemistry v7.1.1 (Roine, 2011). Polyvanadates were excluded from the calculation.

Between a pH of 3 and 13 and above a vanadium concentration of 0.001 mol/L, vanadate ions will polymerise forming $V_2O_7^{4-}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$ and eventually, the decavanadate ion, $H_nV_{10}O_{28}^{(6-n)-}$ (Evans, 1966; Kepert, 1972). The decavanadate ion is known to occur naturally in minerals such as pascoite ($Ca_3(V_{10}O_{28}).17H_2O$) and hummerite ($K_2Mg_2(V_{10}O_{28}).16H_2O$) (Hughes et al., 2002; 2005). Calculations indicate that polyvanadates are the dominant vanadium species from pH 3-5 when the vanadium concentration is 0.001 mol/L at 25°C (Figure 7).

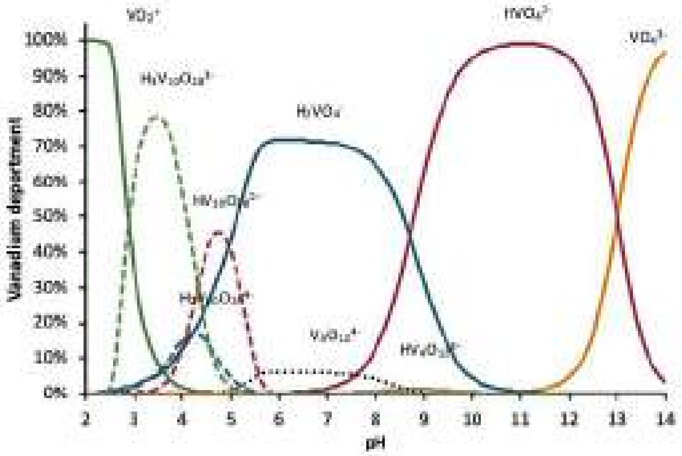


Figure 7. Vanadium deportment from pH 2-14 at 0.001 mol/L V5+. Calculated with Visual Minteq v3.1 (Gustafsson, 2016). The list of species used to generate this diagram was based on a diagram by Kepert (1972). Note: the total vanadium does not add up to 100% between pH 4.0 and 9.5, as the solubility of vanadium is less than 0.001 M over this range.

2.3.2 Gangue element solubility and stable species

Chromium and titanium are frequently present in ores containing vanadium and may be converted to sodium compounds along with vanadium in the salt roasting process. Depending on the conditions in the post-roast leaching stage, these elements may dissolve along with vanadium. Chromium is only soluble under strongly oxidising conditions unless the pH is below 2 or above 10. Titanium is only soluble under strongly acidic conditions (Figure 8). Sodium silicates formed during roasting will also dissolve during leaching, and this soluble silica will need to be removed.

2.3.3 Leaching from roasted material

Whether vanadium ores are roasted with sodium carbonate, chloride, sulphate or hydroxides, the product of the roasting process is always some form of sodium vanadate. Around neutral pH, sodium metavanadate will dissolve in water, forming dihydrogenvanadate ions.

$$NaVO_3 + H_2O \rightarrow H_2VO_4^- + Na^+$$

Reaction 21

Sodium pyro- and orthovanadate will dissolve through similar reactions.

$$Na_4V_2O_7 + H_2O \rightarrow 2\ HVO_4^{2-} + 4\ Na^+$$

Reaction 22

$$Na_3VO_4 \rightarrow VO_4^{3-} + 3\ Na^+$$

Reaction 23

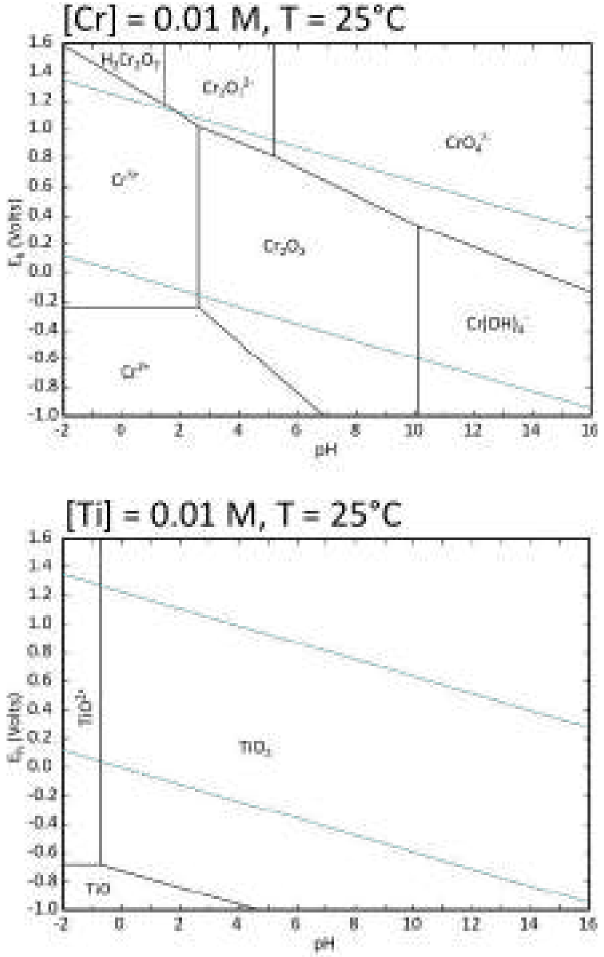


Figure 8. Pourbaix diagram showing the distribution of chromium (top) and titanium (bottom) species in a 0.01 mol/L solution at 25°C produced in HSC Chemistry v7.1.1 (Roine, 2011).

Calculations with HSC Chemistry v7.1.1 (Roine, 2011) indicate that sodium vanadates with higher Na/V ratios will dissolve more readily than sodium metavanadate. Temperature does not have a large effect on the solubility of these compounds. Note that $H_2VO_4^-$ formed through Reaction 21 is stable around pH 6-8, HVO_4^{2-} from Reaction 22 is stable around pH 8-13 and VO_4^{3-} from Reaction 23 is stable at pH > 13 (Figure 6 and Figure 7).

If too little sodium is added during roasting however, Na-V bronzes may form. These compounds have Na/V ratios <1, with some of the vanadium in an oxidation state below 5 (Gupta and Krishnamurthy, 1992). The solubilities of these Na/V bronzes are low, so their formation should be avoided.

$$Na_{0.27}V_2O_5 + 2.46\ H_2O \rightarrow 1.73\ H_2VO_4^- + 0.27\ VO_2 + 1.46\ H^+ + 0.27\ Na^+$$

Reaction 24

Other sodium compounds will dissolve as well, assuming that they were formed during the roasting process. Calculations indicate that the dissolution of titanium is significantly less thermodynamically favourable than that of chromium or vanadium. The dissolution of NaFeO2 without acid is extremely unfavourable (ΔG° > +200 kJ/mol between 20 and 150°C), instead it is more likely to convert to Fe2O3 or FeOOH releasing NaOH into solution.

$$Na_2CrO_4 \rightarrow CrO_4^{2-} + 2\ Na^+$$

Reaction 25

$$Na_2TiO_3 + H_2O \rightarrow TiO_2 + 2\ Na^+ + 2\ OH^-$$

Reaction 26

$$Na_2TiO_3 + 3\ H_2O \rightarrow Ti(OH)_4^0 + 2\ Na^+ + 2\ OH^-$$

Reaction 27

$$Na_2SiO_3 + H_2O \rightarrow H_2SiO_4^{2-} + 2\ Na^+$$

Reaction 28

$$Na_2SiO_3 + 3\ H_2O \rightarrow H_4SiO_4^0 + 2\ Na^+ + 2\ OH^-$$

Reaction 29

$$NaFeO_2 + 2\ H_2O \rightarrow Fe^{3+} + Na^+ + 4\ OH^-$$

Reaction 30

$$2\ NaFeO_2 + H_2O \rightarrow Fe_2O_3 + 2\ Na^+ + 2\ OH^-$$

Reaction 31

$$NaAlO_2 + 2\ H_2O \rightarrow +\ Na^+ + Al(OH)_4^-$$

Reaction 32

2.3.4 Direct leaching of vanadium slag

Direct oxidative leaching has been tested for the recovery of vanadium from slag (Liu et al., 2016). Vanadium is oxidised and converted to soluble vanadium species (Reaction 33).

$$V_2O3_+ + H_2O + 4Fe^{3+} \rightarrow 2VO_2^+ + 2H^+ + 4Fe^{2+} \qquad \text{Reaction 33}$$

Liu et al. (2016) used a pair of electrodes 20 mm apart to oxidise iron and manganese in solution. The addition of manganese sulphate improved the vanadium extraction when the electrodes were active, but otherwise had a slight detrimental effect on the vanadium extraction.

2.3.5 Direct leaching of vanadium ores/concentrates

Vanadium can also be directly leached from titanomagnetite ores, although intense conditions are required. Zhu et al. (2016) leached vanadium-bearing titanomagnetite ore from Shanxi province in China with H_2SO_4 and CaF_2. The fluorite additive generates hydrofluoric acid (Reaction 34), which attacks silica and iron oxides in the ore (Reaction 35, Reaction 36).

$$CaF_2 + 2H^+ + SO_4^{2-} + 2H_2O \rightarrow 2\ HF + CaSO_4.2H_2O \qquad \text{Reaction 34}$$

$$6\ HF + SiO_2 \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O \qquad \text{Reaction 35}$$

$$10\ HF + Fe_2O_3 \rightarrow 2\ FeF_5^{2-} + 4H^+ + 3H_2O \qquad \text{Reaction 36}$$

The ore was ground to 90% passing 74 µm and leached at 95°C for 3 h with a solution/solid ratio of 3 mL/g. Tests were performed in triplicate. Increasing the fluorite addition beyond 5% by mass did not have a significant effect on the vanadium extraction. Likewise, there were minimal improvements in vanadium extraction with increased sulphuric acid once the acid concentration exceeded 5 mol/L (Zhu et al., 2016).

2.3.6 Leaching of uranium-vanadium ores

During the leaching of uranium/vanadium ores, both uranium and vanadium are dissolved together (Reaction 37). Vanadium requires more intense conditions (i.e. higher temperature and acid dosage) to be extracted compared to uranium (Merritt, 1971).

$$K_2(UO_2)_2(V_2O_8).3H_2O + 4\ HSO_4^- + 2H^+ \rightarrow 2K^+ + 2UO_2(SO_4)_2^{2-} + 2H_3VO_4 + 3H_2O$$

Reaction 37

After the leached slurry has been filtered, it passes through two stages of solvent extraction. Uranium is recovered in the first stage and vanadium is recovered in the second. Some pH and Eh adjustment is necessary to prepare the barren uranium liquor for vanadium solvent extraction. Vanadium can then be precipitated as ammonium metavanadate and calcined to produce vanadium pentoxide (Merritt, 1971; IAEA, 1993) as is done in many salt-roast/water-leach processes. Alternatively, uranium can be recovered from the residue following a salt-roast/water leach process for vanadium extraction (Gupta and Krishnamurthy, 1992).

2.4 Alternative processes and sources

Zhao et al. (2014) proposed an alternative method for the recovery of vanadium, chromium and titanium from titanomagnetite ores (Figure 9). The ore is roasted under reducing conditions to selectively reduce iron. The iron is then removed by magnetic separation, and the non-magnetic material leached in hydrochloric acid. This process also enables the recovery of a titanium dioxide by-product (Zhao et al., 2014). The production of by-products such as titanium dioxide, iron metal or chromium together with vanadium could improve the economics of a project.

The optimum C/Fe ratio for roasting was 0.8 (Figure 10, after Zhao et al., 2014). Adding more carbon led to the formation of chromium and vanadium carbides. If too little carbon was added however, the amount of residual iron oxides in the non-magnetic material significantly increased the acid consumption during the leaching step (Zhao et al., 2014).

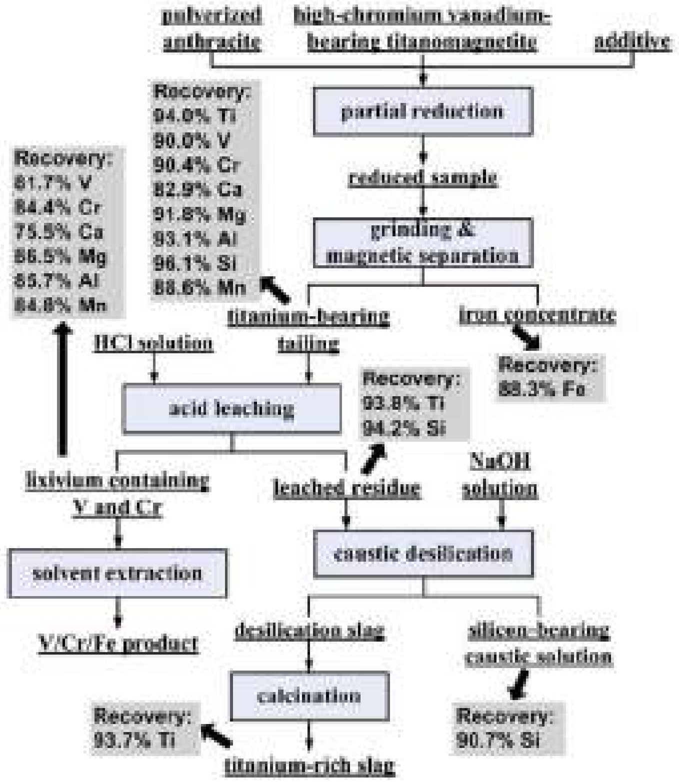


Figure 9. Flowsheet for the reducing roast-HCl leach method from Zhao et al. (2014).

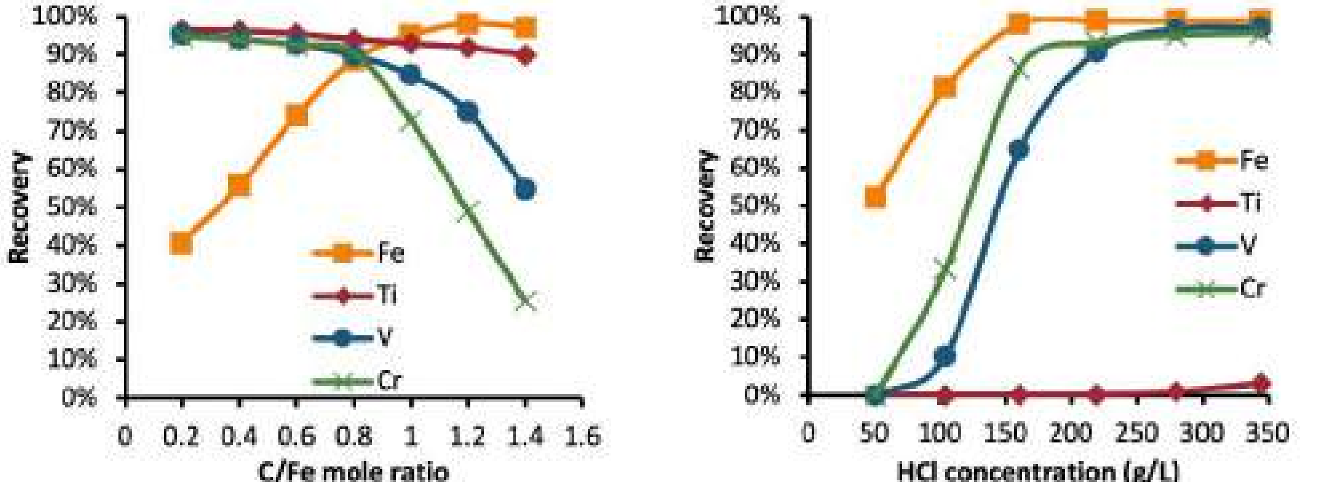


Figure 10. Left: Recovery of metals as a function of C/Fe mole ratio. Conditions: 1200°C, 2h roast, 2.5% Na2CO3. Right: extraction of metals as a function of HCl concentration. Conditions: 5.5:1 liquid to solid ratio by mass, 150°C, 4h leach. Feed material for the leach was prepared by roasting with a C/Fe mole ratio of 0.8.

Navarro et al. (2007) succeeded in extracting vanadium from oil fly ash with both sulphuric acid and sodium hydroxide lixiviants. In addition to the economic benefit of recovering valuable material from a waste product, this also had the effect of reducing the toxicity of the fly ash, making it easier to dispose of.

Russell et al. (1982) extracted vanadium from phosphate ore tailings through a sodium chloride roast-sulphuric acid leach process. Roast temperature, duration and salt dosage were varied. Up to 95% of the vanadium could be extracted by this process (roasting with 10% NaCl for 180 minutes at 845°C). When roasting without the addition of sodium chloride, the maximum vanadium extraction was 79% (roasting for 175 minutes at 775°C). Despite the lower vanadium extractions, Russell et al. (1982) considered the chloride-free option to be more practical, citing corrosion issues arising from the presence of chloride in the leach liquors, and the need to remove chlorides from the solution at the end of the process.

2.5 Vanadium liquor purification

During leaching, deleterious substances such as silica may be dissolved along with the vanadium. These species need to be removed before recovering the vanadium product.

It may also be necessary to increase the concentration of vanadium in the liquor to improve the efficiency of downstream precipitation processes. Many vanadium ores also contain chromium, which can either be a valuable by-product or a dangerous pollutant. In either case, chromium has to be separated from vanadium. Solvent extraction processes have proven effective for this.

2.5.1 Impurity removal

During the salt roasting process, some of the silica in the ore, concentrate or slag will be converted into water soluble sodium silicate. This can dissolve along with the vanadium in the subsequent leaching stage. Soluble silica can interfere with solvent extraction through the formation of crud (Ritcey, 2006).

Alum is effective for silica removal at pH 3.0-3.5 following the water leaching of roasted vanadium ores. The addition of a flocculent will aid in silica removal after the addition of aluminium sulphate (Queneau and Berthold, 1985). Aluminium sulphate and sulphuric acid were used for desilication of vanadium leach liquors following a salt roast/water leach process at Windimurra in Australia (Swinbourne et al., 2016), Mustavaara in Finland (Hukkanen and Walden, 1985), and at other plants elsewhere in the world.

2.5.2 Solvent extraction

Vanadium solutions can be purified by solvent extraction with amine collectors (Lozano and Godinez, 2003; Ning et al., 2014). Alklylphosphoric acids have been shown to be effective for the extraction of vanadium in the tetravalent state and are commonly applied to the solvent extraction of rare earth elements and uranium (Ritcey and Ashbrook, 1979). However some adjustment to the pH and Eh is needed between the uranium and the vanadium solvent extraction when both elements are leached together (Merritt, 1971).

Cationic amine-based extractants bind to anionic vanadates. Wen et al. (2017) derived the following reactions for the loading of vanadate ions into the organic phase with amine extractant N1923, (C10H21)2CHNH2 (Reaction 38-Reaction 40).

$$\frac{4}{3}RN_2 + H_2VO_4^- + H^+ \rightarrow (RNH_2)_{\frac{4}{3}} (H_3VO_4)_{(org)} \qquad \text{Reaction 38}$$

$\log K = 10.94$

$$2\,RNH_2 + V_3O_9^{3-} + 3\,H^+ \rightarrow (RNH_2)_2(H_3V_3O_9)_{(org)} \qquad \text{Reaction 39}$$

$\log K = 25.06$

$$3\,RNH_2 + 0.82\,HV_{10}O_{28}^{5-} + 0.18\,V_{10}O_{28}^{6-} + 5.18\,H^+ \rightarrow (RNH_2)_3(H_6V_{10}O_{28})_{(org)} \qquad \text{Reaction 40}$$

$\log K = 35.10$

Note that R in the three reactions above is $(C_{10}H_{21})_2CH$- (Wen et al., 2017).

The vanadium-loaded organic can then be stripped with ammonia (Lozano and Juan, 2001) or sodium hydroxide (Ning et al., 2014). An example of a stripping reaction based on Reaction 39 is:

$$(RNH_2)_2(H_3V_3O_9)_{(org)} + 3OH^- \rightarrow 2\,RNH_2 + V_3O_9^{3-} + 3\,H_2O \qquad \text{Reaction 41}$$

The primary amine collector LK-N21 has been shown to be effective for the selective loading of vanadium as $V_4O_{12}^{4-}$ over chromium as CrO_4^{2-}. Optimum conditions were a starting pH of 5 in the aqueous phase with 15 minutes of contact time (Ning et al., 2014). More recent work with the amine collector N1923 has shown a high level of selectivity for vanadium over chromium with annular centrifugal contactors. Up to 95% of the vanadium could be extracted without the chromium extraction exceeding 1% (Jing et al., 2017).

An ionic liquid composed of the nitrates of Aliquat 336 $(C_8H_{17})_3N^+$-CH_3 and N1923, $(C_nH_{2n+1})_2CHNH_3^+$, n = 9, 10, 11 has also been shown to be effective for selectively loading vanadium from chromium/vanadium solutions (Zhao et al., 2015). The highest degree of selectivity was obtained with a blend containing 40% N1923 by volume. This mixture was most effective at a pH of 9.3, suggesting that $V_4O_{12}^{4-}$ or $V_3O_9^{3-}$ are more strongly extracted than CrO_4^{2-}. Loading efficiency was also shown to be affected by the anions present. Phosphate, nitrate and chloride ions suppressed the extraction of anionic vanadium species while sulphate ions had a negligible effect on vanadium loading (Zhao et al., 2015).

2.6 Product recovery

2.6.1 Vanadium products and purity requirements

Vanadium is typically recovered as vanadium pentoxide or ferrovanadium metal at the mine site. Vanadium pentoxide can be further purified to produce vanadium chemicals and battery electrolytes, or reduced to ferrovanadium. Ferrovanadium is a mixture of iron and vanadium used in the steel industry for the production of vanadium steel. It's usually 80% V by mass (FeV80) but it can be as low as 40% V (Swinbourne et al., 2016).

The cost of vanadium pentoxide in the electrolyte is a significant component of the overall cost of the battery, though the proportion will depend on the capacity of the battery (Skyllas-Kazacos, 2014). While the production of battery electrolytes requires high purity (99.8%) V2O5, low purity (98%) V2O5 has been tested industrially as it is much cheaper. The effects of different impurities on the performance and lifespan of vanadium redox flow batteries are not fully understood however (Choi et al., 2017). Different impurities are known to have different effects – some positive, some negative, while others have no clear effect (Skyllas-Kazacos, 2014). Identifying which impurities have which effects could potentially simplify the vanadium electrolyte supply chain by enabling vanadium producers to remove deleterious impurities earlier in the process and tailor the end product to meet the needs of the battery producers. Another option would be to bypass the precipitation stage altogether with an aim towards direct conversion of leach liquor to battery grade electrolyte solution.

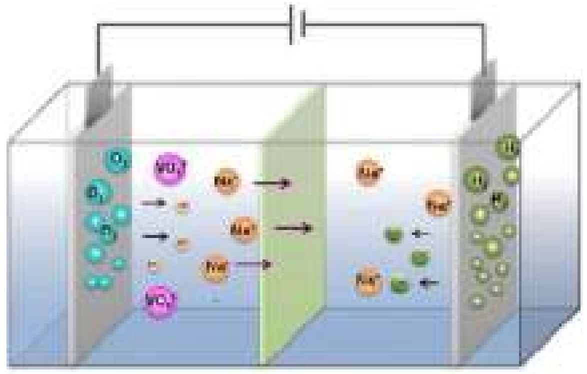


Figure 11. Schematic of the membrane assisted electrochemical cell used by Pan et al. (2017) to separate sodium from sodium vanadate solutions. Illustration from Pan et al. (2017).

2.6.2 Vanadium precipitation

The solubility of pentavalent vanadium is low around pH 2. The simplest technique for recovering vanadium pentoxide involves acidifying the solution to around pH 2 (Douglas et al., 1968). Vanadium as vanadic acid undergoes hydrolysis and precipitation.

$2\,H_3VO_4 \rightarrow V_2O_5 + 3\,H_2O$ **Reaction 42**

In practice, the precipitate is typically of the composition $Na_2H_2V_6O17$-$NaH_3V_6O_{17}$. Adding an excess of acid will speed up precipitation, but ultimately lead to a lower recovery as the solubility of vanadium is increased at lower pH (Douglas et al., 1968).

Since pentavalent vanadium forms an insoluble compound with ammonia, vanadium can also be recovered from solution by precipitating it as ammonium metavanadate, NH_4VO_3 (Goso et al., 2016). This technique is widely used for vanadium recovery in industry (Swinbourne et al., 2016; Hukkanen and Walden, 1985; Rohrmann, 1985)

$H_2VO_4^- + NH_4^+ \rightarrow NH_4VO_3 + H_2O$ **Reaction 43**

Both of these techniques can potentially be improved by using membrane electrolysis approaches. One such process recently proposed by Pan et al. (2017) was developed to recover vanadium from alkaline leach solutions. This process starts with an alkaline sodium orthovanadate solution at pH 13.7. Sodium ions migrate through the membrane, leaving vanadate ions on the anodic side (Figure 11). As hydrogen ions are produced at the anode through the oxidation of water, the pH eventually decreases to 1.8, at which point vanadium can be recovered as $NaHV_6O_{16}$. Advantages of the membrane-based electrolysis approach over the alternatives include higher product purity - 92.6% V2O5 compared to 86.3% by acid precipitation - as well as avoiding the need for ammonia, a potential environmental hazard (Pan et al., 2017). The higher the purity of the vanadium product, the easier it is to convert to high purity vanadium compounds suitable for redox flow battery electrolytes.

2.6.3 Vanadium pentoxide production

After filtration and drying, ammonium metavanadate can be converted to vanadium pentoxide by calcination, driving off water and ammonia.

$2\,NH_4VO_3 \rightarrow V_2O_5 + H_2O_{(g)} + 2\,NH_{3(g)}$ **Reaction 44**

A variant of this process uses a reducing atmosphere to produce vanadium trioxide instead. This is typically done when the vanadium is to be further converted to ferrovanadium onsite, as it requires less reductant in the final stage (Swinbourne et al., 2016).

$2\,NH_4VO_3 + 2\,CO_{(g)} \rightarrow V_2O_3 + H_2O_{(g)} + 2\,NH_{3(g)} + 2\,CO_{2(g)}$ **Reaction 45**

2.6.4 Vanadium/ferrovanadium metal production

It is difficult to reduce vanadium, chromium and titanium carbothermically, as these metals tend to form carbides (Rosenqvist, 1983). Vanadium metal is produced by aluminothermic reduction of vanadium oxide. This is usually done in the presence of iron, forming ferrovanadium (Swinbourne et al., 2016).

$3\,V_2O_5 + 10\,Al \rightarrow 6\,V + 5\,Al_2O_3$ **Reaction 46**

The aluminium requirements can be decreased by carrying out the calcination/deammoniation process in a reducing environment to produce V_2O_3 instead (Swinbourne et al., 2016).

$3\,V_2O_3 + 6\,Al \rightarrow 6\,V + 3\,Al_2O_3$ **Reaction 47**

Aluminium reduction can also be used to produce ferrovanadium from vanadium-rich steel refining slag, although the reaction is quite violent, resulting in difficulties with temperature control (Lindvall and Ye, 2012). Ferrosilicon is sometimes used for these purposes as well. Howard et al. (1992) tested both reductants on a sample of vanadium slag and determined aluminium to be the superior reductant.

A molten salt electrolysis process can also be used to produce metallic vanadium. Weng et al. (2016) have shown that this method can be used to directly reduce sodium metavanadate to metallic vanadium in a mixed $CaCl_2$/NaCl system. They succeeded in reducing sodium metavanadate to vanadium trioxide in sodium chloride media, however further reduction was only possible in the mixed calcium/sodium chloride mixture.

$CaV_2O_6 + 4e^- \rightarrow CaV_2O_4 + 2O^{2-}$ **Reaction 48**

$CaV_2O_4 + 6e^- \rightarrow CaO + 2V + 3O^{2-}$ **Reaction 49**

Operating the cell with a voltage of 3.0 V was sufficient to reduce vanadium to the metallic state although increasing the voltage to 3.5 V resulted in the formation of vanadium carbide, VC (Weng et al. 2016).

2.6.5 By-product recovery from leach liquors

Earlier, it was mentioned that other metals may be converted to water soluble sodium salts during vanadium recovery processes (Reaction 9-Reaction 14). While solvent extraction is effective for the separation of vanadium from chromium, an older and simpler approach of reducing chromium to the trivalent state is effective as well. Cole and Breitenstein (1951) used SO_2 and Na_2CO_3 to recover chromium as a by-product after hydrolytic precipitation of vanadium at pH 2.5 and 95°C. Na_2CO_3 is added to bring the pH up to 6.5, while SO_2 reduces chromium to the trivalent state which subsequently precipitates as $Cr(OH)_3$. This can then be converted to Cr_2O_3 by calcination.

$2\,CrO_4^{2-} + 2\,H_2O + 3\,SO_{2(g)} + 2\,OH^- \rightarrow 2\,Cr(OH)_3 + 3\,SO_4^{2-}$ **Reaction 50**

$2\,Cr(OH)_3 \rightarrow Cr_2O_3 + 3\,H_2O_{(g)}$ **Reaction 51**

3 SALT ROASTING PROCESS OPTIONS

Vanadium roasting processes rely on the conversion of vanadium minerals to water soluble sodium metavanadate, $NaVO_3$. This is typically achieved by roasting with sodium carbonate or sodium chloride, although there are alternatives. The reactions between sodium carbonate and various vanadium minerals were shown in Section 3.1.1. The reactions with vanadium trioxide and the other sodium compounds are as follows:

$V_2O_3 + 2\ NaOH + O_2 \rightarrow 2\ NaVO_3 + H_2O$ **Reaction 52**

$V_2O_3 + 2\ NaCl + O_2 + H_2O \rightarrow 2\ NaVO_3 + 2\ HCl$ **Reaction 53**

$V_2O_3 + Na_2SO_4 + O_2 \rightarrow 2\ NaVO_3 + SO_3$ **Reaction 54**

Calcium and magnesium oxides may also form vanadate compounds.

$CaO + V_2O_3 + O_2 \rightarrow CaV_2O_6$ **Reaction 55**

$MgO + V_2O_3 + O_2 \rightarrow MgV_2O_6$ **Reaction 56**

The Gibbs free energy values for the formation of various metavanadate compounds from vanadium trioxide with different compounds are compared in Figure 12.

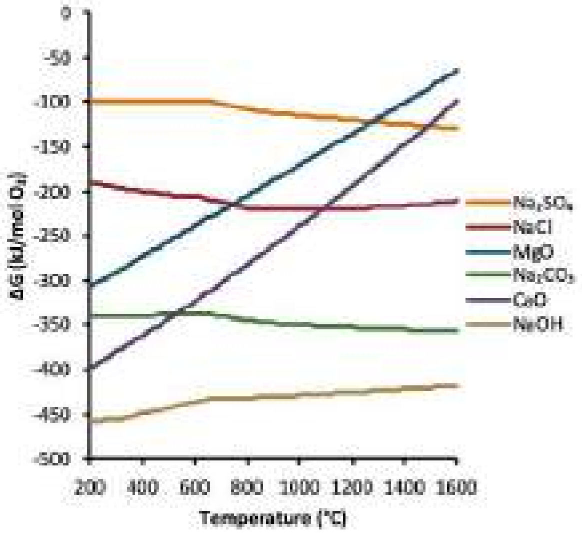


Figure 12. Ellingham diagram for the formation of Na/Mg/Ca metavanadate from vanadium trioxide with different compounds (Reaction 4; Reaction 52-Reaction 56).

3.1 Carbonate roasting

The use of sodium carbonate for vanadium roasting avoids the emission of harmful corrosive gases such as SO2, HCl or Cl2 that are emitted when sodium chloride or sulphate are used, making the sodium carbonate roasting process cleaner than the alternatives (Li et al., 2015). The alkalinity of sodium carbonate helps to attack the spinel structure of magnetite and coulsonite (Goddard and Fox, 1981).

3.1.1 Thermodynamics of carbonate roasting

The conversion of vanadium and chromium oxides to sodium metavanadate and chromate is thermochemically as well as kinetically more favourable at higher temperatures. Vanadium oxides are more readily converted however than chromium oxides, as illustrated in Figure 13, which shows the effect of temperature on the free energy of conversion of the relevant phases of these two elements. In addition, the conversion of Fe2O3 to NaFeO2 is not thermodynamically favourable until the temperature exceeds 1100°C so it is excluded from the diagram.

Other sodium vanadates may be formed if higher sodium dosages are added. Calculations indicate that this is also more favourable at higher temperatures, provided that sufficient sodium is available.

3.1.2 Effect of temperature

At lower temperatures, the extent of vanadium oxidation may be too low. If the temperature is too high however, sintering may occur inhibiting the diffusion of oxygen (Zhang et al., 2015). Sintering may also occur as a result of excessive sodium salt addition (Rohrmann, 1985). The optimum roasting temperature will vary depending on the vanadium source. Vanadium can be recovered from slag at lower temperatures than are required for the roasting of vanadium magnetite concentrates. The optimum temperature for vanadium recovery from concentrate was 1100°C and 950°C for vanadium recovery from slag (Figure 14, after Gabra and Malinsky, 1981).

Other slags may be roasted at lower temperatures. Li et al. (2011b) found that the leaching recovery of vanadium from slag following roasting decreased once the roasting temperature exceeded 700°C. Silitonga and Prosser (1976) determined the optimum temperature for vanadium recovery from slag by sodium carbonate roasting to be 800°C. Slag was roasted with a slag/Na_2CO_3 ratio of 10:3 and a particle size distribution of 100% passing 74 µm and 50% passing 50 µm. After roasting, the slag was quenched and leached in water (50 mL water/10 g slag) at 80°C for up to 24 hours. At most, it took 4 hours of leaching for the limiting extraction to be reached (Silitonga and Prosser, 1976).

Jena et al. (1995) determined the optimum roasting temperature for vanadium recovery from slag produced by smelting a vanadium-rich magnetite concentrate was 950°C.

Coulsonite can be converted to sodium metavanadate at a lower temperature than is normally required for roasting titanomagnetite ores (van Vuuren and Stander, 2001). Van Vuuren and Stander (2001) succeeded in converting coulsonite to water soluble sodium vanadates at temperatures of ~600°C, below the typical roasting temperature of 1000-1100°C.

Rapidly cooling the calcine can improve the rate of recovery. Quenching after roasting (22.5-30% Na_2CO_3, 1025°C) resulted in increased chromium and vanadium extraction when leaching a Canadian titaniferous magnetite ore (Lucas and Ritcey, 1980).

The optimum temperature for chromium extraction is higher than that for vanadium extraction (Gabra and Malinsky, 1981), as might be expected based on the thermodynamic data presented earlier (Figure 13). By controlling the temperature and other parameters, it is possible to selectively convert vanadium oxides while minimising the conversion of chromium oxides in a vanadium/chromium slag. Chromium can then be converted and recovered in a second roasting/leaching stage (Figure 15 after Li et al., 2015).

Temperature control is important in the subsequent leaching process as well. Shahnazi et al. (2012) extracted vanadium from LD converter slag by leaching with sodium hydroxide solutions between 25 and 70°C after roasting 200 g slag with 50 g Na_2CO_3 at 1000°C for 2 h. Increasing the leaching temperature above 50°C did not significantly affect the leaching recovery however.

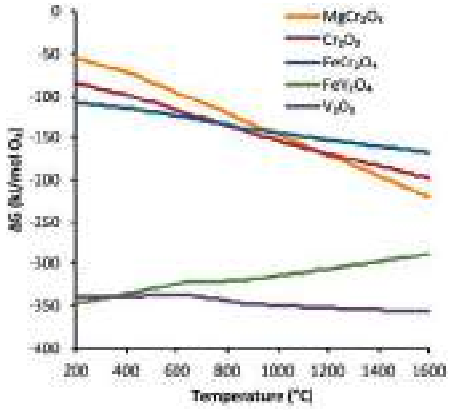


Figure 13. Ellingham diagram of the conversion of various oxides to $NaVO_3$ or Na_2CrO_4 by roasting with Na_2CO_3 and the stoichiometric amount of oxygen (Reaction 4, Reaction 5, Reaction 9 - Reaction 11). When present, iron and magnesium are included as Fe2O3 and MgO in the products. Calculated using HSC Chemistry v7.1.1 (Roine, 2011).

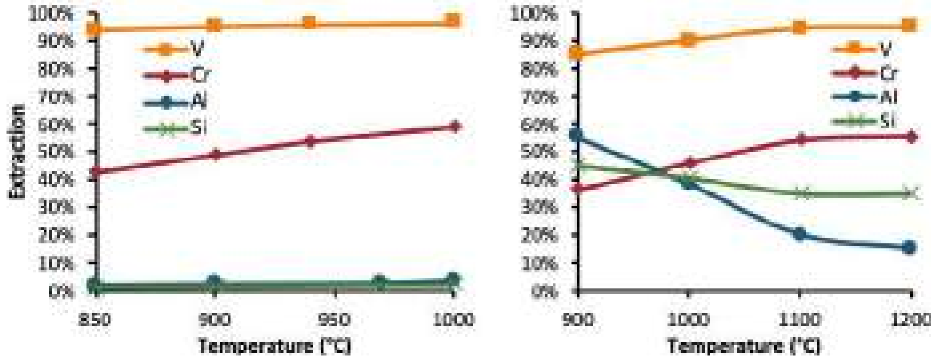


Figure 14. Recovery of various elements as a function of temperature from slag (left) and concentrate (right) after Gabra and Malinsky (1981). Slag ground to -200 µm was roasted for 60 minutes with 20% Na_2CO_3 and leached for 60 minutes at 5% solids. Concentrate was ground to -42 µm and roasted for 60 minutes with 10% Na_2CO_3 and leached for 60 minutes at 5% solids.

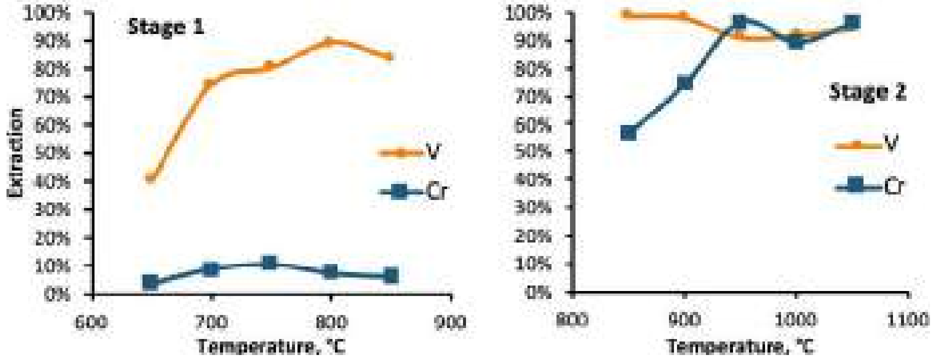


Figure 15. Vanadium and chromium extraction from slag roasted and leached in two stages. Stage 1: Roasting at 650-850°C for 120 minutes with a Na/V ratio of 3.3 followed by leaching at 90°C for 60 minutes with a liquid/solid ratio of 10:1. Stage 2: Roasting at 850-1050°C for 120 minutes with a Na/(V+Cr) ratio of 5 followed by leaching at 25°C for 30 minutes with a liquid/solid ratio of 5:1. Data from Li et al. (2015).

3.1.3 Effect of reagent dosage

By restricting the sodium carbonate dose, it is possible to selectivelyconvert vanadium to sodium metavanadate without converting chromium to sodium chromate (Li et al., 2015). The same approach can be used to minimise the conversion of undesirable elements to water soluble sodium salts (Gabra and Malinsky, 1981). As the conversion of V2O3 to $NaVO_3$ is more thermodynamically favourable than the conversion of Cr_2O_3 to Na_2CrO_4 (Figure 13), it occurs at a lower sodium carbonate dosage (Figure 16, Figure 17).

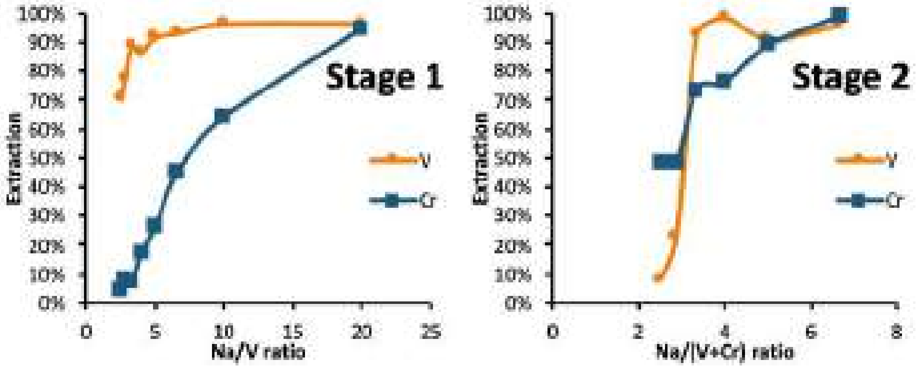


Figure 16. Vanadium and chromium extraction from slag roasted and leached in 2 stages. Stage 1: Roast at 800°C for 120 min with a Na/V ratio of 2.5-20 followed by leach at 90°C for 60 min with a liquid/solid ratio of 10:1. Stage 2: Roast at 950°C for 120 min with a Na/(V+Cr) ratio of 2.5-6.7 followed by leach at 25°C for 30 min with a liquid/solid ratio of 5:1. Data from Li et al. (2015).

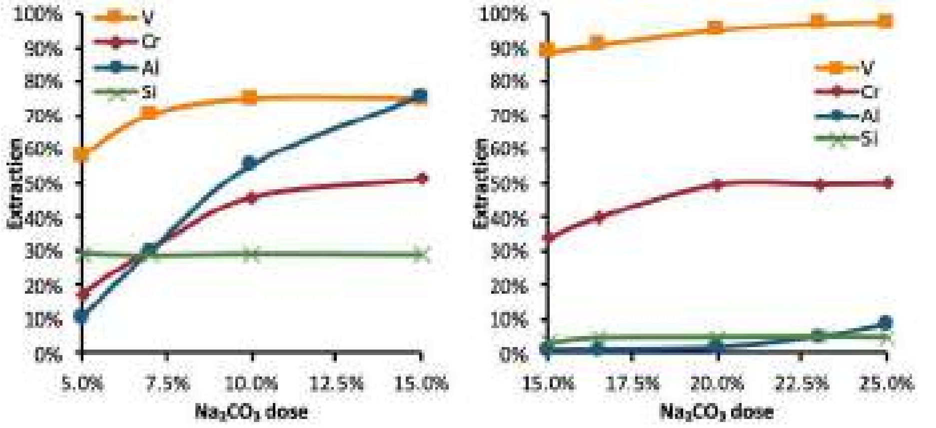


Figure 17. Recovery of various elements as a function of sodium carbonate dosage from concentrate (left) and slag (right) at 900°C after Gabra and Malinsky (1981). Concentrate was ground to -42 µm and slag ground to -200 µm. Both were roasted for 60 minutes and leached for 60 minutes at 5% solids.

A higher Na_2CO_3 dose results in a higher extraction. More carbonate is required when processing slags with greater silica content (Hitching and Kelly, 1982). Adding too much sodium carbonate may be detrimental to the process however. High Na2CO3/concentrate ratios can lead to the formation of deposits on the walls of the kiln, as was observed at the Windimurra vanadium mine (Swinbourne et al., 2016).

3.1.4 Effect of particle size

Particle size has a large effect on the recovery of vanadium from roasted concentrate, but negligible effect on vanadium leaching extraction from roasted slag. Concentrates require much finer grinding for effective vanadium extraction (Gabra and Malinsky, 1981). If the concentrate is ground too finely however, excessive amounts of concentrate may be blown out of the kiln during roasting (Connelly et al., 2008). Working with very finely ground material (<44 µm), Lucas and Ritcey (1980) found that further grinding had no significant effect on the recovery of vanadium or chromium from titaniferous magnetite.

3.1.5 Influence of gangue elements in the feed

The presence of calcium, magnesium, iron and aluminium can lead to the formation of insoluble vanadates (Goso et al., 2016). Calcite in the ore can decompose to calcium oxide during salt roasting, subsequently forming insoluble calcium vanadates/uranates during the salt roasting of uranium-vanadium ores (Merritt, 1971, chapter 5).

$CaCO_3 \rightarrow CaO + CO_2$ Reaction 57

$CaO + V_2O_5 \rightarrow CaV_2O_6$ Reaction 58

$MgO + V_2O_5 \rightarrow MgV_2O_6$ Reaction 59

$CaO + UO_3 \rightarrow CaUO_4$ Reaction 60

Calcium vanadate will dissolve in carbonate solutions however (Merritt, 1971), so the calcined material should be leached in carbonate solutions rather than water if calcium vanadate is expected to form. Calcium oxides may also be used as an additive in the salt roasting process.

Alternatively, the formation of calcium vanadate can be supressed with the addition of sodium phosphate or pyrite prior to roasting. Calcium will react to form calcium phosphate or sulphate instead of calcium vanadate (Shahnazi et al., 2012). Silica can also mitigate the deleterious effects of lime, through the formation of calcium silicate (Gupta and Krishnamurthy, 1992).

It is important to reject silica during beneficiation prior to roasting (Swinbourne et al., 2016). One method to do this is by re-grinding the magnetic concentrate and using reverse flotation with amine collectors to remove silica (Connelly et al., 2008). Silica consumes sodium carbonate during roasting. Silica can also form glassy silicates containing insoluble vanadium, and the formation of low-melting sodium silicates can result in fusion occurring and inhibit the oxidation of vanadium. Aegerine, NaFeSi2O6, formed from iron and silica can incorporate vanadium into its structure, rendering it insoluble (Goddard and Fox, 1981). Reduced water leach recoveries tend to occur when the silica content of the kiln feed exceeds 2.2% (Connelly et al., 2008).

The formation these silicates is mainly a problem when roasting under alkaline conditions (Gupta and Krishnamurthy, 1992). The addition of alumina or cryolite to the roast can mitigate the effects of silica on vanadium recovery (Goddard and Fox, 1981).

Hitching and Kelly (1982) investigated the salt roasting and water leaching of several steel flushing slags from New Zealand. Higher amounts of silica in the slag reduced the vanadium extraction. Vanadium extraction dropped sharply once the SiO2 content exceeded 14% (Figure 18).

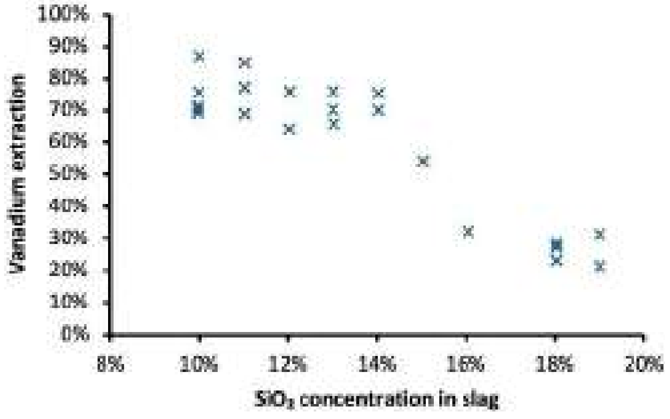


Figure 18. Vanadium extraction from different slags vs. SiO_2 content during water leaching after roasting with 20% Na_2CO_3 at 850°C for three hours, data extracted from Hitching and Kelly (1982).

3.2 Sodium chloride roasting

The sodium chloride roasting process usually requires water, unlike roasting with sodium carbonate or sulphate. The rate of vanadium conversion is also affected by the concentration of water vapour in the gas stream (Dresher, 1961). Without water, the reaction is slower (Dresher, 1961), less thermodynamically favaourable, will produce chlorine rather than hydrogen chloride as a gaseous product (Reaction 56; Gupta and Krishnamurthy, 1992). The anhydrous process also requires 50% more oxygen per mole of vanadium. Sodium chloride roasting is inferior to carbonate roasting when treating titanomagnetite (Goddard and Fox, 1981).

$$V_2O_3 + 2\,NaCl + O_2 + H_2O_2 \rightarrow NaVO_3 + 2\,HCl \qquad \text{Reaction 61}$$

$$V_2O_3 + 2\,NaCl + 1.5\,O_2 \rightarrow 2\,NaVO_3 + Cl_2 \qquad \text{Reaction 62}$$

Sodium chloride will also react with other vanadium and chromium minerals, forming soluble vanadates and chromates. Reactions for the chloride roasting of coulsonite, chromium trioxide, chromite and magnesiochromite are shown below:

$$FeV_2O_4 + 2\,NaCl + 1.25\,O_2 + H_2O \rightarrow 2\,NaVO_3 + 0.5\,Fe_2O_3 + 2\,HCl_{(g)} \qquad \text{Reaction 63}$$

$$Cr_2O_3 + 4\,NaCl + 1.5\,O_2 + 2\,H_2O \rightarrow 2\,Na_2CrO_4 + 4\,HCl_{(g)} \qquad \text{Reaction 64}$$

$$FeCr_2O_4 + 4\,NaCl + 2\,H_2O + 1.75\,O_2 \rightarrow 2\,Na_2CrO_4 + 0.5\,Fe_2O_3 + 4\,HCl_{(g)} \qquad \text{Reaction 65}$$

$$MgCr_2O_4 + 4\,NaCl + 2\,H_2O + 1.5\,O_2 \rightarrow 2\,Na_2CrO_4 + MgO + 4\,HCl_{(g)} \qquad \text{Reaction 66}$$

3.2.1. Effect of temperature

For the extraction of vanadium from vanadiferous clay from Arkansas, the optimum temperature was 825°C. This is above the melting point of sodium chloride (801°C). It is also worth noting that the sodium chloride dose had minimal effect on the vanadium extraction when roasting at the optimum temperature (Figure 19 after Goddard and Fox, 1981).

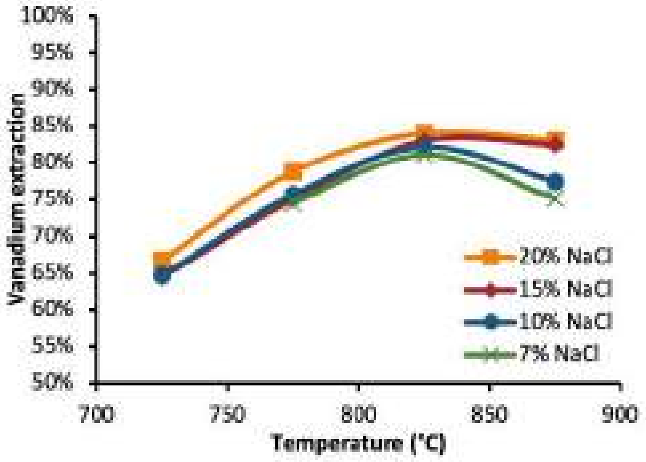


Figure 19. Vanadium extraction vs. temperature for the sodium chloride roasting of vanadiferous clay. Ore was roasted for 2 hours then leached in water for 1 hour. Data extracted from Goddard and Fox (1981).

3.2.2 Effect of reagent dosage

The sodium chloride dosage had minimal effect on the vanadium extraction from vanadiferous clay when roasting took place at the optimum temperature of 825°C (Figure 19). Further tests showed minimal improvement in extraction once the sodium chloride dose exceeded 7% of the ore mass. There was also a decrease in sodium chloride utilisation beyond this point (Figure 20 after Goddard and Fox, 1981).

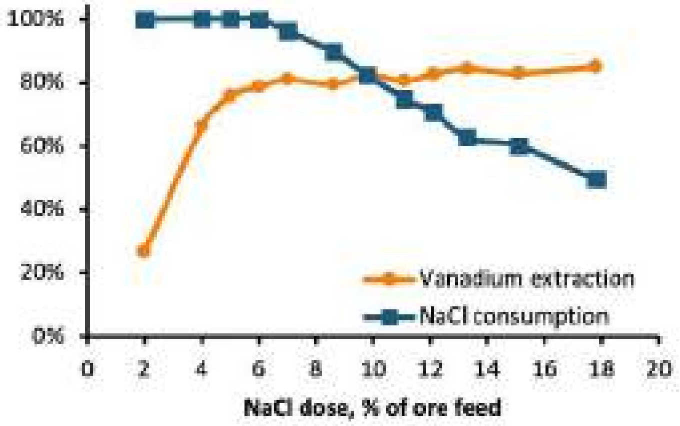


Figure 20. Vanadium extraction and sodium chloride consumption while roasting vanadiferous clay for 2 hours at the optimum temperature of 825°C after Goddard and Fox (1981).

The amount of sodium chloride added can affect the amounts of other reagents needed in downstream processes. Increasing the salt dose in salt roasting of vanadiferous dolomitic shale from Nevada decreased the acid consumption during leaching (Table 1 after Brooks and Potter, 1974). Higher sodium chloride doses also suppressed the formation of soluble silica during roasting (Table 2 after Brooks and Potter, 1974).

TABLE 1. REAGENT DOSAGES FOR ROAST-LEACHING OF VANADIFEROUS SHALE (2 H AT 900°C) AFTER BROOKS AND POTTER (1974).

NACL DOSE (kg/t SHALE)	NACL CONSUMPTION (kg/kg V_2O_5)	H2SO4 CONSUMPTION (kg/kg V_2O_5)
50	7.2	22
100	14.3	10
150	21.5	7

TABLE 2. REAGENT DOSE AND LEACH LIQUOR COMPOSITION FOLLOWING A 3 HOUR ROAST AND A 1 HOUR LEACH (30°C, PH 2.5) AFTER BROOKS AND POTTER (1974)

ROASTING TEMPERATURE (°C)	NACL DOSE (kg/t SHALE)	[V_2O_5] (g/L)	[SIO_2] (g/L)
900	50	6.6	16
900	100	6.3	6.8
925	50	6.5	7.6
925	100	5.6	2.6

TABLE 3. ACID SOLUBLE VANADIUM (50 KG H2SO4/T ROASTED SHALE) IN WEATHERED SHALE AFTER ROASTING (3 H, 900°C) WITH A VARIETY OF CHLORIDES AFTER BROOKS AND POTTER (1974).

SALT	DOSE (kg/t)	V EXTRACTION
None	0	49%
NaCl	50	66%
LiCl	30	72%
KCl	50	76%
$CaCl_2$	50	75%
$AlCl_3$	50	70%

Brooks and Potter (1974) tested various alternatives to sodium chloride for roasting vanadiferous shale from Nevada. Potassium chloride and calcium chloride were both more effective than sodium chloride (Table 3). Roasting with calcium chloride formed large amounts of soluble silica however, so those tests were discontinued (Brooks and Potter 1974).

Sodium chloride has been shown to be more effective than potassium chloride for extracting vanadium from fly ash at 950°C, while potassium chloride was more effective at 750°C. The differences between sodium and potassium chloride were not as clear when the process was run at 850°C (Holloway and Etsell, 2004).

3.2.3 Influence of gangue elements in the feed

While the formation of soluble silica species is expected in carbonate roasting, calculations indicate that the formation of sodium silicate from silica and sodium chloride is unfavourable ($\Delta G° = +102$ kJ/mol at 1000°C). This is a possible advantage of roasting with sodium chloride over sodium carbonate. A higher sodium chloride dose has been shown to supress soluble silica formation (Brooks and Potter, 1974; Table 1; Table 2).

Calcite inhibits vanadium extraction in the salt roasting process, due to the formation of calcium vanadates which are less soluble than sodium vanadates. Over time, calcium vanadates may react with silica in the ore in the presence of sodium chloride, forming sodium vanadates (Reaction 61 and Reaction 62 after Goddard and Fox, 1981).

$$CaV_2O_6 + SiO_2 + 2\ NaCl + H_2O \rightarrow CaSiO_3 + 2\ NaVO_3 + 2\ HCl$$

Reaction 67

$$Ca_2V_2O_7 + 2\ SiO_2 + 2\ NaCl + H_2O \rightarrow 2\ CaSiO_3 + 2\ NaVO_3 + 2\ HCl$$

Reaction 68

3.3 Other salt roasting systems

Sodium oxalate produced as a by-product from the alumina industry was used in the original Windimurra flowsheet, although this later became prohibitively expensive and was not used when the plant later re-opened (Connelly et al., 2008). Thermodynamic calculations with HSC Chemistry v7.1.1 (Roine, 2011) indicate that the reaction between sodium oxalate and vanadium trioxide (Reaction 63) is strongly favourable, even more than sodium hydroxide. Some more common alternatives to sodium carbonate or chloride roasting are discussed below.

$$V_2O_3 + Na_2C_2O_4 + 1.5\ O_2 \rightarrow 2\ NaVO_3 + 2\ CO_2$$

Reaction 69

3.3.1 Sodium sulphate roasting

Sulphate roasting is more selective for vanadium than carbonate roasting, but it requires higher temperatures to be effective (Merritt, 1971). Other downsides include the formation of corrosive sulphur trioxide (Nkosi et al., 2017). Nkosi et al. (2017) determined the optimum temperature for vanadium extraction by sulphate roasting to be 1200°C, higher than is typically effective for carbonate or chloride roasting. Minimal details are available in the open literature on sulphate-based processes for vanadium extraction.

A mixed carbonate/sulphate roast process has been proposed for the Mokopane vanadium project in South Africa, although the details are unknown (Bushveld Minerals, 2017). A similar system was used previously at the Vantra vanadium plant in the same area of South Africa (Rohrmann, 1985)

3.3.2 Sodium hydroxide roasting

While not technically a roasting process as the reaction happens in molten media, the chemistry involved in the sodium hydroxide method for sodium vanadate, chromate and titanate production has a lot in common with that found in salt roasting processes.

3.3.2.1 Molten hydroxide processes

Roasting with anhydrous sodium hydroxide has been tested on chromite/ilmenite ores (Parirenyatwa et al., 2016) and vanadium/titanium slags (Chen et al., 2013; Ji et al., 2017). Comparing the thermodynamics of sodium hydroxide roasting with carbonate roasting, the hydroxide route is more favourable by approximately 100 kJ/mol O_2 (see Figure 12). Chromite reacts with sodium hydroxide and oxygen forming water soluble sodium chromate (Parirenyatwa et al., 2016).

$FeCr_2O_4 + 4\ NaOH + 1.75\ O_2 \rightarrow 0.5\ Fe_2O_3 + 2\ Na_2CrO_4 + 2\ H_2O_{(g)}$ **Reaction 70**

$MgCr_2O_4 + 4\ NaOH + 1.5\ O_2 \rightarrow MgO + 2\ Na_2CrO_4 + 2\ H_2O_{(g)}$ **Reaction 71**

Other spinel phases in the ore will react with sodium hydroxide as well.

$FeAl_2O_4 + 2\ NaOH + 0.25\ O_2 \rightarrow 0.5\ Fe_2O_3 + 2\ NaAlO_2 + H_2O_{(g)}$ **Reaction 72**

$MgAl_2O_4 + 2\ NaOH \rightarrow MgO + 2\ NaAlO_2 + H_2O_{(g)}$ **Reaction 73**

$Fe_3O_4 + 3\ NaOH + 0.25\ O_2 \rightarrow 3\ NaFeO_2 + 1.5\ H_2O_{(g)}$ **Reaction 74**

Similar reactions take place with KOH. The formation of $NaFeO_2$ and $KFeO_2$ in the roasting stage results in the pH rising during the water leaching stage.

$2\ NaFeO_2 + H_2O \rightarrow Fe_2O_3 + 2\ NaOH$ ***Reaction 75***

$2\ KFeO_2 + H_2O \rightarrow Fe_2O_3 + 2\ KOH$ **Reaction 76**

As the thermodynamics are more favourable, conversion is possible at lower temperatures compared to carbonate roasting processes. Sodium hydroxide melts at 323°C (CRC, 2005), so the reaction takes place in molten sodium hydroxide. Rapid conversion of titanium (Chen et al., 2013) and vanadium oxides (Ji et al., 2017) to sodium titanates and vanadates is possible in molten sodium hydroxide media at 500-600°C.

Ji et al. (2017) pressed slag and NaOH into pellets which were roasted at 400-700°C. Tests at 600°C showed higher vanadium extractions for pressed pellets (99%) compared to unconsolidated powder (71%) under the same conditions. There was minimal difference between vanadium extraction at 600 and 700°C after 30 minutes.

Liu et al. (2013) tested a similar roasting process on vanadium and chromium-containing slag at temperatures ranging from 325 to 450°C, with the addition of sodium nitrate as an oxidiser/redox mediator.

$2\ FeV_2O_4 + 12\ NaOH + 5\ NaNO_3 \rightarrow Fe_2O_3 + 4\ Na_3VO_4 + 6\ H_2O + 5\ NaNO_2$ ***Reaction 77***

$2\ FeCr_2O_4 + 8\ NaOH + 7\ NaNO_3 \rightarrow Fe_2O_3 + 4\ Na_2CrO_4 + 4\ H_2O + 7\ NaNO_2$ **Reaction 78**

The presence of sodium hydroxide inhibits the decomposition of sodium nitrite to harmful nitrogen oxide gases (Liu et al., 2013). Sodium nitrate is regenerated by sparging oxygen into the reactor.

$2\ NaNO_{2(l)} + O_2 \rightarrow 2\ NaNO_{3(l)}$ **Reaction 79**

3.3.2.2 Sub-molten salt processes

Another method for vanadium extraction is the sub-molten salt process studied by Wang et al. (2014). This is related to the hydroxide roasting process discussed above, and relies on the reduced melting point of partially hydrated sodium hydroxide. Vanadium slag is combined with 80% NaOH which melts at around 150°C (Pickering, 1893). A flowsheet for the sub-molten salt process is shown in Figure 21.

Up to 90% of the vanadium can be extracted with 80% NaOH at 210°C. Chromium extraction was quite low under these conditions however. Higher extractions for both vanadium and chromium were possible in 80% KOH.

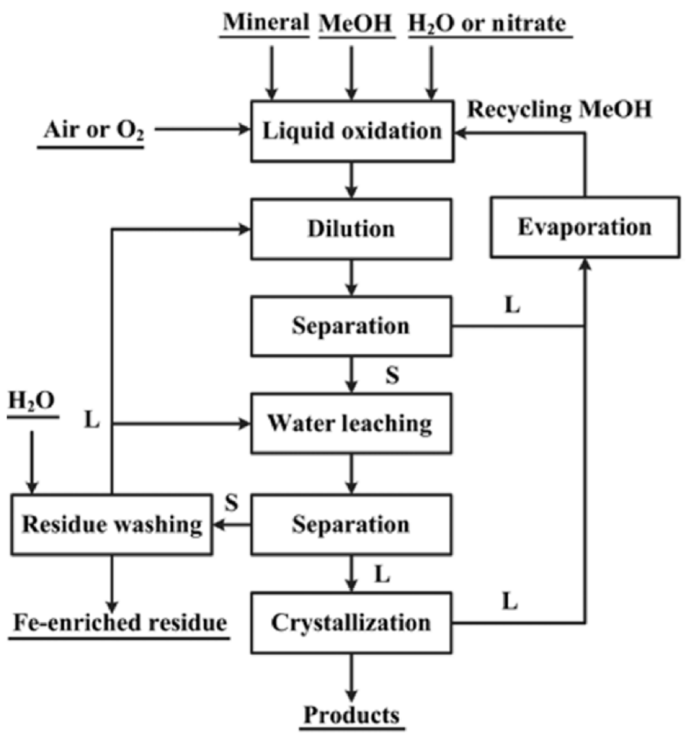


Figure 21. Simplified flowsheet for the sub-molten salt process after Wang et al. (2014).

3.3.3 Lime roasting

Roasting with lime converts vanadium to calcium vanadate (Reaction 49), which can then be leached with sulphuric acid or sodium carbonate. Sodium carbonate reacts with calcium vanadate, forming calcium carbonate and releasing vanadate (Reaction 74). Other vanadates including $Ca_2V_2O_7$ and $Ca_3V_2O_8$ may also form during roasting (Zhang et al., 2015).

$$CaV_2O_6 + CO_3^{2-} + 2\,H_2O \rightarrow CaCO_3 + 2\,H_2VO_4^-$$

Reaction 80

If present in the ores, magnesium and manganese may also form vanadates, although the formation of magnesium and manganese vanadates is less thermodynamically favourable than calcium vanadate. Calculations with HSC Chemistry v7.1.1 indicate that the dissolution of calcium vanadates is more thermodynamically favourable in the presence of carbonate ions than without (Reaction 75, Reaction 76).

$$Ca_nV_2O_{5+n} + (3-n)\,H_2O \rightarrow n\,Ca^{2+} + 2\,H_{(3-n)}VO_4^{n-}$$

Reaction 81

$$Ca_nV_2O_{5+n} + (3-n)\,H_2O + n\,CO_3^{2-} \rightarrow n\,CaCO_3 + 2\,H_{(3-n)}\,VO_4^{n-}$$

Reaction 82

where n = 1, 2, 3.

Sodium carbonate is a much more effective reagent for leaching vanadium than water, when lime is used as the roasting reagent. Holloway and Etsell (2004) roasted vanadiferous oil sand fly ash with varied amounts of lime at different temperatures, and then leached the roasted product in either water or 100 g/L Na2CO3. Sodium carbonate proved to be a much more effective lixiviant regardless of roasting conditions.

Zhang et al. (2015) determined that the optimum temperature for roasting vanadium slag with lime was 850°C. The rate of heating can also affect the vanadium extraction in this process. Vanadium slag in the size range of 48-75 µm was mixed with calcium oxide and pressed into pellets 8-10 mm in diameter. These were heated in a corundum crucible at different rates before quenching and grinding. After grinding, the roasted slag was leached for one hour at 65°C at a pH of 2.5 and stirring rate of 500 rpm. Slower heating during roasting resulted in higher vanadium extraction when the slag was subsequently leached.

Later work by Li et al. (2016) showed that the vanadium recovery process following the roasting of slag with calcium oxide could be simplified by leaching the calcined slag with ammonium carbonate solutions. This lixiviant selectively recovers vanadium without dissolving undesirable impurities such as phosphorus.

$$CaV_2O_6 + (NH_4)_2CO_{3(aq)} \rightarrow CaCO_3 + 2\,NH_4VO_{3(aq)}$$

Reaction 83

On cooling, vanadium precipitates from the leach solution as ammonium metavanadate and the leach liquor can be recycled for use in further leaching processes (Li et al., 2017). The solubility of ammonium metavanadate is lower at lower temperatures.

3.3.4 Microwave roasting processes

In recent years, the metallurgical applications of microwaves have been the subject of many studies, particularly in China. Microwaves can replace conventional furnaces as a heating mechanism, and have been shown to be more effective in a number of applications including spodumene calcination for lithium extraction (Salakjani et al., 2017) among other pyrometallurgical processes (Pickles, 2009).

Microwave treatments have also been shown to improve the efficiency of grinding and mineral separation processes. Differing degrees of thermal expansion among different phases generates cracks at grain boundaries, improving the liberation when the ore is milled. This has been shown to be effective for separating magnetite from ilmenite (Guo et al., 2011). Difficulties in separating magnetite from ilmenite have been known to cause problems in beneficiating vanadium-bearing titanomagnetite ores (Connelly et al., 2008)

When applied to vanadium slag, microwave roasting resulted in faster conversion at lower temperature. The different mode of heating resulted in particles with a greater porosity (Figure 22 after Zhang et al., 2016a). While Zhang et al. (2016a) didn't leach the roasted material, it is likely that leaching would be faster for more porous particles.

Roasting vanadium slag in a microwave furnace significantly improved the rate of vanadium extraction from the slag when it was subsequently leached with sulphuric acid. Zhang et al. (2016b) roasted vanadium slag from the Panzhihua area of Sichuan province, China. Slag was ground to -75 µm and roasted in a microwave furnace for 10 minutes at the set temperature ±50°C. Roasting at temperatures above 350°C was detrimental to the vanadium extraction.

Microwaves are effective for extracting vanadium from stone coal as well. Vanadium extraction is faster and more effective at a lower temperature when compared to conventional roasting techniques. When the stone coal is subsequently leached, leaching is faster and requires less sulphuric acid for the same degree of vanadium extraction (Wang et al., 2015; Yuan et al., 2015).

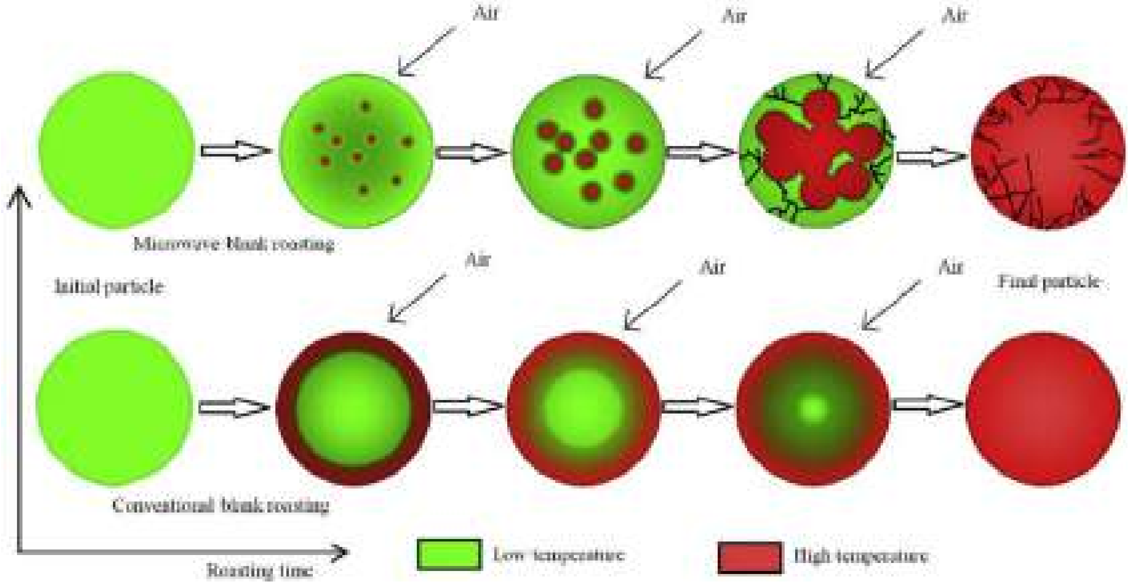


Figure 22. Comparison of microwave heating and conventional heating after Zhang et al. (2016a).

4 CONCLUSIONS

While roasting with sodium carbonate remains the dominant process for extracting vanadium from titanomagnetites, some alternative processes have been shown to be equally effective in recent years. Substituting sodium hydroxide for sodium carbonate for instance, allows vanadium recovery at lower temperatures, i.e., 500°C with sodium hydroxide compared to over 800°C with sodium carbonate. Dissolving vanadium in molten sodium hydroxide, on the other hand, is effective at even lower temperatures of 325-450°C.

A reducing roast process has been shown to be effective for separating iron from vanadium, titanium and chromium in titanomagnetites, enabling the production of separate vanadium, titanium, chromium, and iron products. Considering the historical variations in the vanadium price, projects that produce multiple commodities along with vanadium have clear economic advantages over those producing vanadium alone. The production of multiple commodities from titanomagnetites is thus worthy of further investigation to secure reliable sources of vanadium and titanium.

Microwave-based processes have also shown promising results in various metallurgical studies, including some studies on vanadium ores and magnetite. Roasting vanadium-bearing slag in a microwave results in faster conversion compared to roasting in a conventional furnace. Microwaves have applications earlier in the process as well. Microwave treatment before grinding has been shown to be effective for separating ilmenite from magnetite, potentially enabling the production of higher grade concentrates from titanomagnetite ores.

In the final stages of the process, membrane electrolysis has been demonstrated to be an effective approach for separating sodium from vanadium in sodium vanadate solutions, allowing ammonia to be eliminated from the process and potential reagent recovery. The higher product purity achievable by this process also offers the potential advantage to simplify the further purifying into vanadium compounds suitable for use in flow batteries.

With battery applications expected to entail a bigger share of the vanadium market in the coming years, it is worth investigating how to improve the process as a whole, so as to simplify the production of high purity vanadium precoursor salts and solutions suitable to electrolyte production for use in redox flow batteries. If a sufficiently pure vanadium solution could be produced from vanadium leach liquors directly by solvent extraction or some other processes, the conventional precipitation/calcination process could be bypassed, hence reducing the energy inputs and environmental impact of vanadium electrolyte production. Moreover, success in the development of direct ore to electrolyte processing technology could greatly simplify the vanadium supply chain and consequently reduce the production cost and environmental impact of vanadium redox flow batteries, paving the way for even wider application.

5 REFERENCES

1. Algar, V. 2017. Investing in the energy storage future. http://www.resourcesrisingstars.com.au/sites/default/files/Vanadium%20Australia%20-%20RRS%20Presentation%20-%202017.pdf (accessed 25/08/2017)

2. Anon, 2011. Vanadium Sector review. http://www.tngltd.com.au/images/tngltd—-vujaiquoos.pdf (accessed 10/07/2017)

3. Balan, E.; De Villiers, J.P.; Eeckhout, S.G.; Glatzel, P.; Toplis, M.J.; Fritsch, E.; Allard, T.; Galoisy, L.; Calas, G., 2006. The oxidation state of vanadium in titanomagnetite from layered basic intrusions. American Mineralogist, 91(5-6), 953-956

4. Barote, L., R. Weissbach, R. Teodorescu, C. Marinescu, and M. Cirstea. 2008. Stand-alone wind system with vanadium redox battery energy storage. In: Optimization of Electrical and Electronic Equipment, 2008. OPTIM 2008. 11th International Conference on, pp. 407-412. IEEE, 2008.

5. Bindi, L.; Cámara, F.; Griffin, W. L.; Huang, J-X.; Gain, S. E. M.; Toledo, V.; O'Reilly, S. Y. 2019. Discovery of the first natural hydride. American Mineralogist, 104, 611-614

6. Brooks, P. T.; Potter, G. M. 1974. Recovering Vanadium from Dolomitic Nevada Shale. U.S. Bureau of Mines, Report of investigations 7932

7. Bushveld Minerals. 2017. http://www.bushveldminerals.com/Vanadium.aspx (Accessed 13/09/2017)

8. Cámara, F.; Bindi, L.; Pagano, A.; Pagano, R.; Gain, S. E. M.; Griffin, W. L. 2019. Dellagiustaite: A Novel Natural Spinel Containing V2+. Minerals 2019, 9, 4; doi:10.3390/min9010004

9. Chaudary, H.; Miller, D. M.; Brungs, M. P.; Relton, G. R. 1997. Redox chemistry of vanadium in molten binary silicates and slags. In: The 5th International Conference on Molten Slags, Fluxes and Salts, January 5-8, 1997, Sydney, Australia

10. Chen, D; Zhao, L.; Liu, Y.; Qi, T.; Wang, J.; Wang, L. 2013. A novel process for recovery of iron, titanium, and vanadium from titanomagnetite concentrates: NaOH molten salt roasting and water leaching processes. Journal of Hazardous Materials, 244-245, 588-595

11. Choi, C.; Kim, S.; Kim, R.; Choi, Y.; Kim, S.; Jung, H-Y.; Yang, J. H.; Kim, H-T. 2017. A review of vanadium electrolytes for vanadium redox flow batteries. Renewable and Sustainable Energy Reviews 69, 263-274

12. Cole, S. S.; Breitenstein, J. S. 1951. Recovery of Vanadium from Titaniferous Magnetite. Journal of Metals (New York) 3, 1133-1137

13. Connelly, D.; Reed, C.; Palmer, R. 2008. Trends with Titaniferous Magnetite Processing for Vanadium Extraction. In: Metallurgical Plant Design and Operating Strategies (MetPlant 2008) 18 - 19 August 2008 Perth, WA, p419-431

14. CRC. 2005. The CRC Handbook of Chemistry and Physics, 85th edition.

15. Dechaine, G. P.; Gray, M. R. 2010. Chemistry and Association of Vanadium Compounds in Heavy Oil and Bitumen, and Implications for Their Selective Removal. Energy Fuels, 24, 2795-2808

16. Dill, H. G. 2010. The "chessboard" classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. Earth Science Reviews, 100, 1-420

17. Douglas, D. A.; Bovey, W. D.; Temple, D. A. 1968. A process for the production of high grade vanadium pentoxide from solutions containing chromium and silica. Journal of the Southern African Institute of Mining and Metallurgy 68 (9), 385-396

18. Dresher, W. H. 1961. A mechanism study of the formation of sodium vanadate compounds under the conditions of the salt-roast process.

19. Evans Jr, H.T., 1966. The molecular structure of the isopoly complex ion, decavanadate (V10O286-). Inorganic Chemistry, 5(6), 967-977.

20. Gabra, G.; Malinsky, I. 1981. A comparative study of the extraction of vanadium from titaniferous magnetite and slag. In: Extractive metallurgy of refractory metals, The Metallurgical Society of AIME, edited by H. Y. Sohn, O. Norman Carlson, J. Thomas Smith, p167-189

21. García-Labiano, F.; de Diego, L. F.; Cabello, A.; Gayán, P.; Abad, A.; Adánez, J.; Sprachmann, G. 2016. Sulphuric acid production via Chemical Looping Combustion of elemental sulphur. Applied Energy 178, p736-745

22. Geoscience Australia. 2014. Australia's Identified Mineral Resources 2013. Geoscience Australia, Canberra. http://dx.doi.org/10.11636/1327-1466.2013

23. Goddard, J. B.; Fox, J. S. 1981. Salt roasting of vanadium ores. In: Extractive metallurgy of refractory metals, The Metallurgical Society of AIME, edited by H. Y. Sohn, O. Norman Carlson, J. Thomas Smith, p127-145

24. Goso, X. C.; Lagendijk, H.; Erwee, M.; Khosa, G. 2016. Indicative Vanadium Deportment in the Processing of Titaniferous Magnetite by the Roast-Leach and Electric Furnace Smelting Processes. In: Hydrometallurgy Conference 2016, The Southern African Institute of Mining and Metallurgy, p69-79

25. Guo, S. H.; Chen, G.; Peng, J. H.; Chen, J.; Li, D. B.; Liu, L. J. 2011. Microwave assisted grinding of ilmenite ore. Transactions of the Nonferrous Metals Society of China, 21, 2122-2126

26. Gupta, C. K.; Krishnamurthy, N. 1992. Extractive Metallurgy of Vanadium, Elsevier Science Publishers B. V.

27. Gustafsson, J. P. 2016. Visual Minteq. Version 3.1., Stockholm, Sweden

28. Habteselassie , M. M.; Mathison, C. I.; Gilkes, R. J. (1996) Vanadium in magnetite gabbros and its behaviour during lateritic weathering, Windimurra Complex, Western Australia, Australian Journal of Earth Sciences, 43:5, 555-566

29. Hausen, D. M. 1984. Process mineralogy of the Na2O-V2O5 system in vanadium production. In: Process Mineralogy III, p235-246

30. Henning. 2013. Stonehenge Metals corporate presentation. Australian Uranium and Rare-Earths Conference, Fremantle, July 2013

31. Hitching, K. D.; Kelly, E. G. 1982. Extraction of Vanadium from N.Z. Steel Slags using a Salt-roast/leach Process. Proceedings of the AusIMM, 283, 37-42

32. Holloway, P. C.; Etsell, T. H. 2004. Recovery of vanadium from oil sands fly ash using potassium and calcium reagents. In: Waste Processing and Recycling in Mineral and Metallurgical Industries V.

33. Howard, R. L.; Richards, S. R.; Welch, B. J.; Moore, J. J. 1992. Pyrometallurgical Processing of Vanadiferous Slag Using Plasma/Induction Heating. In: INFACON 6. Proceedings of the 6th International Ferroalloys Congress, Cape Town. Volume 1. Johannesburg, SAIMM, 1992, p 225-231

34. Hughes, J. M.; Schindler, M.; Rakovan, J.; Cureton, F. E. 2002. The crystal structure of hummerite, KMg(V5O14).8H2O: Bonding between the [V10O28]6- structural unit and the {K2Mg2(H2O)16}6+ interstitial complex. The Canadian Mineralogist 40, 1429-1435

35. Hughes, J. M.; Schindler, M.; Francis, C. A. 2005. The C2/m disordered structure of pascoite, Ca3[V10O28].17H2O: Bonding between structural units and interstitial complexes in compounds containing the [V10O28]6- decavanadate polyanion. The Canadian Mineralogist 43, 1379-1386

36. Hukkanen, E.; Walden, H. 1985. The production of vanadium and steel from titanomagnetites. International Journal of Mineral Processing, 15, 89-102

37. IAEA, 1993. Uranium Extraction Technology. International Atomic Energy Agency, Vienna, 1993

38. Inoue, R.; Suito, H. 1982. Distribution of vanadium between liquid iron and MgO saturated slags of the system CaO-MgO-FeOx-SiO2. Transactions of the Iron and Steel Institute of Japan, 22, 705-714

39. Jena, B. C.; Dresler, W.; Reilly, I. G. 1995. Extraction of titanium, vanadium and iron from titanomagnetite deposits at Pipestone Lake, Manitoba, Canada. Minerals Engineering 8 (1/2), 159-168

40. Ji, Y.; Shen, S.; Liu, J.; Xue. 2017. Cleaner and effective process for extracting vanadium from vanadium slag by using an innovative three-phase roasting reaction. Journal of Cleaner Production 149, 1068-1078

41. Jing, X.; Ning, P.; Cao, H.; Sun, Z.; Wang, J. 2017. Separation of V(V) and Cr(VI) in leaching solution using annular centrifugal contactors. Chemical Engineering Journal 315, 373-381

42. Judd, J. C.; Sandberg, R. G.; Huiatt, J. L. 1986. Recovery of Vanadium, Uranium and Phosphate From Idaho Phosphorite Ores. United States Department of the Interior, Bureau of Mines, Report of Investigations 9025

43. Kelley, K.D., Scott, C.T., Polyak, D.E., and Kimball, B.E., 2017, Vanadium, chap. U of Schulz, K.J., DeYoung, J.H., Jr., Seal, R.R., II, and Bradley, D.C., eds., Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply: U.S. Geological Survey Professional Paper 1802, p. U1–U36, https://doi.org/10.3133/pp1802U.

44. Kelly, B. F. 1993. Vanadium recovery at BHP New Zealand Steel Limited, Glenbrook, New Zealand. In: Australasian mining and metallurgy : the Sir Maurice Mawby memorial volume. Edited by J.T. Woodcock and J.K. Hamilton, p1245-1247

45. Kepert, D. L., 1972. The Early Transition Metals, Academic Press Inc., London.

46. Kim, J-H; Cho, H-C; Han, K. 2014. Leaching behavior of U and V from a Korean uranium ore using Na2CO3 and KOH. Geosystem Engineering, 17:2, 113-119

47. Largo Resources. 2016. Corporate Presentation. https://www.slideshare.net/Largoresources/largo-corporate-presentation-may-2016 (Accessed 12/09/2017)

48. Lauf, R. J. 2016. Mineralogy of Uranium and Thorium. Schiffer Publishing, Pennsylvania.

49. Leont'ev, L. I.; Shavrin, S. V. 2000. The iron-ore base of Russia and problems with the processing of titanomagnetites. Metallurgist, 44 (3-4), 169-170

50. Lewis, S. E.; Henderson, R. A.; Dickens, G. R.; Shields, G. A.; Coxhell, S. 2010. The geochemistry of primary and weathered oil shale and coquina across the Julia Creek vanadium deposit (Queensland, Australia). Miner Deposita, 45, 599-620

51. Li, L., Kim, S., Wang, W., Vijayakumar, M., Nie, Z., Chen, B., Zhang, J., Xia, G., Hu, J., Graff, G., Liu, J. and Yang, Z. 2011a. A Stable Vanadium Redox-Flow Battery with High Energy Density for Large-Scale Energy Storage. Advanced Energy Materials, 1, 394–400

52. Li, X S,.; Bing, X. I. E.; Wang, G. E.; Li, X. J. 2011b. Oxidation process of low-grade vanadium slag in presence of Na2CO3. Transactions of the Nonferrous Metals Society of China. 21.8, 1860-1867

53. Li, H-Y.; Fang, H-X.; Wang, K.; Zhou, W.; Yang, Z.; Yan, X-M.; Ge, W-S.; Li, Q-W.; Xie, B. 2015. Asynchronous extraction of vanadium and chromium from vanadium slag by stepwise sodium roasting–water leaching. Hydrometallurgy 156, 124-135

54. Li, H. Y.; Wang, K.; Hua, W. H.; Yang, Z.; Zhou, W.; Xie, B. 2016. Selective leaching of vanadium in calcification-roasted vanadium slag by ammonium carbonate. Hydrometallurgy 160, 18-25

55. Li, M.; Liu, B.; Zheng, S.; Wang, S.; Du, H.; Dreisinger, D. B.; Zhang, Y. 2017. A cleaner vanadium extraction method featuring non-salt roasting and ammonium bicarbonate leaching. Journal of Cleaner Production 149, 206-217

56. Lindvall, M.; Ye, G. 2012. Experiences of using various metallurgical reactors for reduction of vanadium bearing steel slags and other wastes. In: International Smelting Technology Symposium (Incorporating the 6th Advances in Sulfide Smelting Symposium). Edited by J. P. Downey, T. P. Battle and J. F. White. TMS (The Minerals, Metals & Materials Society), 2012

57. Liu, S.; Jaireth, S. 2011. Exploring for calcrete-hosted uranium deposits in the Paterson region, Western Australia. AusGeo News, 103 September 2011, 1-5. http://www.ga.gov.au/webtemp/image_cache/GA19878.pdf (accessed 25/08/2017)

58. Liu, B.; Du, H.; Wang, S. N.; Zhang, Y.; Zheng, S. L.; Li, L. J.; Chen, D. H. 2013.A Novel Method to Extract Vanadium and Chromium from Vanadium Slag using Molten NaOH-NaNO3 Binary System. Journal of the American Institute of Chemical Engineers, 59 (2), 541-552

59. Liu, Z.; Li, Y.; Chen, M.; Nueraihemaiti, A.; Du, J.; Fan, X.; Tao, C-Y. 2016. Enhanced leaching of vanadium slag in acidic solution by electro-oxidation. Hydrometallurgy 159, 1-5

60. Lozano, L. J.; Godinez, C. 2003. Comparative study of solvent extraction of vanadium from sulphate solutions by primene 81R and alamine 336. Minerals Engineering 16, 291-294

61. Lozano, L.J; Juan, D. 2001. Solvent extraction of polyvanadates from sulphate solutions by primene 81R. Its application to the recovery of vanadium from spent sulphuric acid catalysts leaching solutions, Solvent Extraction and Ion Exchange, 19 (4), 659-676

62. Lucas, B. H.; Ritcey, G. M. 1980. An alkaline roast-leach process for treatment of titaniferous magnetite for recovery of chromium, vanadium & aluminium. CIM Bulletin, September 1980, 126-132

63. Merritt, R. C. 1971. The extractive metallurgy of Uranium. Colorado School of Mines Research Institute, Golden, Colorado

64. Moskalyk, R. R.; Alfantazi, A. M. 2003. Processing of vanadium: a review. Minerals Engineering, 16, 793-805

65. Navarro, R.; Guzman, J.; Saucedo, I.; Revilla, J.; Guibal, E. 2007. Vanadium recovery from oil fly ash by leaching, precipitation and solvent extraction processes. Waste Management, 27, 425-438

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

67. Nkosi, S.; Dire, P.; Nyambeni, N.; Goso, X. C. 2017. A comparative study of vanadium recovery from titaniferous magnetite using salt, sulphate, and soda ash roast-leach processes. In: 3rd Young Professionals Conference, The Southern African Institute of Mining and Metallurgy, p 191-200

68. Pan, B.; Jin, W.; Liu, B.; Zheng, S.; Wang, S.; Du, H.; Zhang, Y. 2017. Cleaner production of vanadium oxides by cation-exchange membrane-assisted electrolysis of sodium vanadate solution. Hydrometallurgy 169, 440-446

69. Parirenyatwa, S.; Escudero-Castjon, L.; Sanchez-Segado, S.; Hara, Y.; Jha, A. 2016. Comparative study of alkali roasting and leaching of chromite ores and titaniferous minerals. Hydrometallurgy 165, 213-226

70. Perles, T. 2016. Vanadium Corp presentation. https://www.dropbox.com/s/kixp7ig8srh9kn6/S16-01_Perles_an.pdf?dl=0 (Accessed 25/09//2017).

71. Pickering, S.U., 1893. LXI.—The hydrates of sodium, potassium, and lithium hydroxides. Journal of the Chemical Society, Transactions, 63, 890-909.

72. Pickles, C.. A. 2009. Microwaves in extractive metallurgy: Part 2 – A review of applications. Minerals Engineering 22, 1112-1118

73. Polyak, D. E. 2016. Vanadium. In: USGS Minerals Yearbook 2015. U.S. Department of the Interior, U.S. Geological Survey

74. Protean Energy, 2019. Daejon Vanadium Mining Study Update. https://wcsecure.weblink.com.au/pdf/POW/02082657.pdf (accessed 03/06/2019)

75. Queneau, P. B.; Berthold, C. E. 1985. Silica in Hydrometallurgy: An Overview. In: Impurity Control and Disposal. CIM Metallurgical Society, 15th Annual Hydrometallurgical Meeting

76. Radtke, A. S. 1962. Coulsonite, FeV2O4, a Spinel-type Mineral from Lovelock, Nevada. The American Mineralogist 47 (12), 1284-1291

77. Raja, B.V., 2007. Vanadium market in the world. Steel world, 13(2), 19-22

78. Ressel, R.; Hochenhofer, M.; Antrekowitsch, H. 2005. Processing of vanadiferous residues to ferrovanadium. EPD Congress 2005, TMS, p763-778

79. Reznitsky, L. Z.; Sklyarov, E. V.; Suvorova, L. F.; Karmanov, N. S.; Ushchapovskaya, Z. F. 2005. The Chromite-Coulsonite-Magnetite Solid Solution: The First Find of a Rare Variety of Spinel in Terrestrial Rocks. Doklady Earth Sciences, 404 (7) 1121-1125

80. Ritcey, G. M. 2006. Solvent Extraction – Principles and Applications to Process Metallurgy, Second Edition, Volume 1. G. M. Ritcey and Associates Incorporated

81. Ritcey, G. M.; Ashbrook, A. W. 1979. Solvent Extraction – Principles and Applications to Process Metallurgy Volume 2. Elsevier Science Publishers B. V.

82. Robiette, A. G. E. 1973. Electric Smelting Processes. Halsted Press

83. Rohrmann, B. 1985. Vanadium in South Africa. Journal of the Southern African Institute of Mining and Metallurgy 85, 141-150

84. Roine, A. 2011. Chemical reaction and Equilibrium Software. Version 7.1.1., Outotec, Research Centre, Pori, Finland

85. Rosenqvist, T. 1983. Principles of extractive metallurgy

86. Russell, J. H.; Collins, D. G.; Rule, A. R. 1982. Vanadium Roast-Leach Dissolution From Western Phosphate Tailings. United States Department of the Interior, Bureau of Mines, Report of Investigations 8695

87. Salakjani, N. Kh.; Nikoloski, A. N.; Singh, P. 2017. Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 2: Microwave heating. Minerals Engineering 100, 191-199

88. Schuiling, R. D.; Feenstra, A. 1980. Geochemical behaviour of vanadium in iron-titanium oxides. Chemical Geology, 30, 143-150

89. Schwertmann, U.; Pfab, G. 1996. Structural vanadium and chromium in lateritic iron oxides: Genetic implications. Geochimica et Cosmochimica Acta, 60 (21), 4279-4283

90. Shahnazi, A.; Rashchi, F.; Zahidi, E. 2012. A Kinetics Study on the Hydrometallurgical Recovery of Vanadium from LD Converter Slag in Alkaline Media. EPD Congress 2012, TMS, p425-433

91. Skyllas-Kazacos, M. 2014. Vanadium Electrolyte Cost and Purity Considerations for Vanadium Redox Flow Battery Applications. COM 2014 - Conference of Metallurgists Proceedings ISBN: 978-1-926872-24-7

92. Skyllas-Kazacos, M.; Chakrabarti, M. H.; Hajimolana, S. A.; Mjalli, F. S.; Saleem, M. 2011. Progress in Flow Battery Research and Development. Journal of The Electrochemical Society, 158 (8) R55-R79

93. Silitonga, M.; Prosser, A. P. 1976. The chemistry of vanadium losses in the alkali-roast process. Proceedings of the AusIMM 259, 13-18

94. Smirnov, L. A.; Tret'yakov, M. A.; Gladyshev, V. I. 2001. Processing vanadium-bearing titanomagnetites at the Nizhny Tagil Metallurgical Combine. Metallurgist, 45 (5-6), 232-234

95. Steinberg, W. S.; Geyser, W.; Nell., J. 2011. The history and development of the pyrometallurgical processes at Evraz Highveld Steel & Vanadium. Journal of the Southern African Institute of Mining and Metallurgy 111 (10), 705-710

96. Swinbourne, D. R.; Richardson, T.; Cabalteja, F. 2016. Understanding ferrovanadium smelting through computational thermodynamics modelling. Mineral Processing and Extractive Metallurgy, 125 (1), 45-55

97. Taipale, K. J. A. 2013. Composition of magnetite in gabbros of the Mustavaara Fe-Ti-V Deposit. MSc thesis, Oulu University, Finland

98. UniEnergy Technologies. 2016. UniEnergy Technologies Strategic Partner to Deliver World's Largest Battery. http://www.uetechnologies.com/news/72-unienergy-technologies-strategic-partner-to-deliver-world-s-largest-battery (Accessed 29/09/2017)

99. Van Vuuren, C. P. J.; Stander, P. P. 2001. Technical note: The oxidation of FeV2O4 by oxygen in a sodium carbonate mixture. Minerals Engineering 14 (7), 803-808

100. Vitolo, S.; Seggiani, M.; Filippi, S.; Brocchini, C. 2000. Recovery of vanadium from heavy oil and Orimulsion fly ashes. Hydrometallurgy, 57, 141-149

101. Wang, Z. H.; Zheng, S. L.; Wang, S. N.; Liu, B.; Wang, D. W.; Zhang, Y. 2014. Research and prospect on extraction of vanadium from vanadium slag by liquid oxidation technologies. Transactions of the Nonferrous Metals Society of China. 24, 1273-1288

102. Wang, M.; Xian, P.; Wang, X.; Li, B. 2015. Extraction of Vanadium from Stone Coal by Microwave Assisted Sulfation Roasting. JOM 67 (2), 369-374

103. Wen, J.; Liu, F.; Cao, H.; Ning, P.; Zhang, Y. 2017. Insights into the extraction of various vanadium species by primary amine. Hydrometallurgy 173, 57-62

104. Weng, W.; Wang, M.; Gong, X.; Wang, Z.; Wang, D.; Guo, Z. 2016. One-step electrochemical preparation of metallic vanadium from sodium metavanadate in molten chlorides. International Journal of Refractory Metals and Hard Materials 55, 47-53

105. Wenk, H., Bulakh, A. 2004. Minerals, Their constitution and origin. Cambridge University Press

106. Xu, C.; Zhang, Y.; Liu, T.; Huang, J. 2017. Characterization and Pre-Concentration of Low-Grade Vanadium-Titanium Magnetite Ore. Minerals 7 (8), 137.

107. Yan, J. R.; Xie, B.; Zeng, X. Y.; Huang, Q. Y.; Li, H. Y. 2013. Vanadium Distribution Between Blast Furnace Slag and Hot Metal. In: The 4th International Symposium on High-Temperature Metallurgical Processing. Edited by T. Jiang, J. Y. Hwang, P. J. Mackey, O. Yucel, G. Zhou. TMS (The Minerals, Metals & Materials Society), p 333-339

108. Yuan, Y.Z.; Zhang, Y.M.; Liu, T.; Chen, T.J., 2015. Comparison of the mechanisms of microwave roasting and conventional roasting and of their effects on vanadium extraction from stone coal. International Journal of Minerals, Metallurgy, and Materials, 22(5), 476-482.

109. Zhang, J.; Zhang, W.; Zhang, L.; Gu, S. 2015. Mechanism of vanadium slag roasting with calcium oxide. International Journal of Mineral Processing 138, 20-29

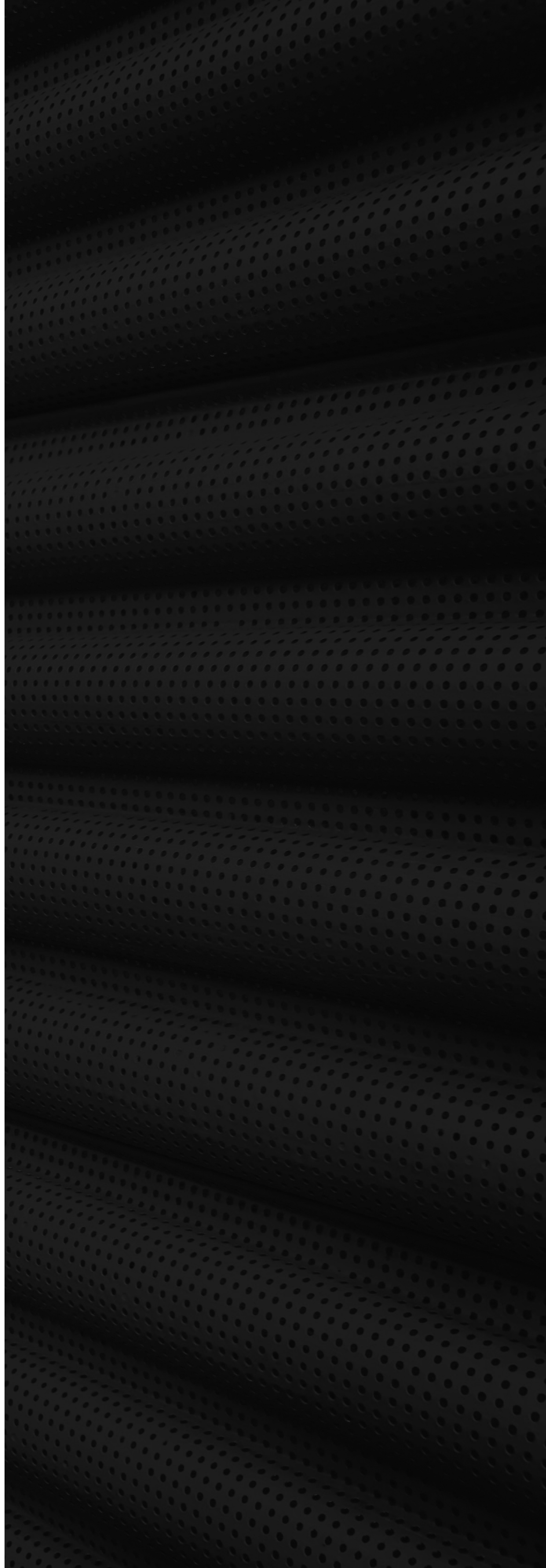
110. Zhang, X.; Liu, F.; Xue, X.; Jiang, T. 2016a. Effects of microwave and conventional blank roasting on oxidation behavior, microstructure and surface morphology of vanadium slag with high chromium content. Journal of Alloys and Compounds 686, 356-365

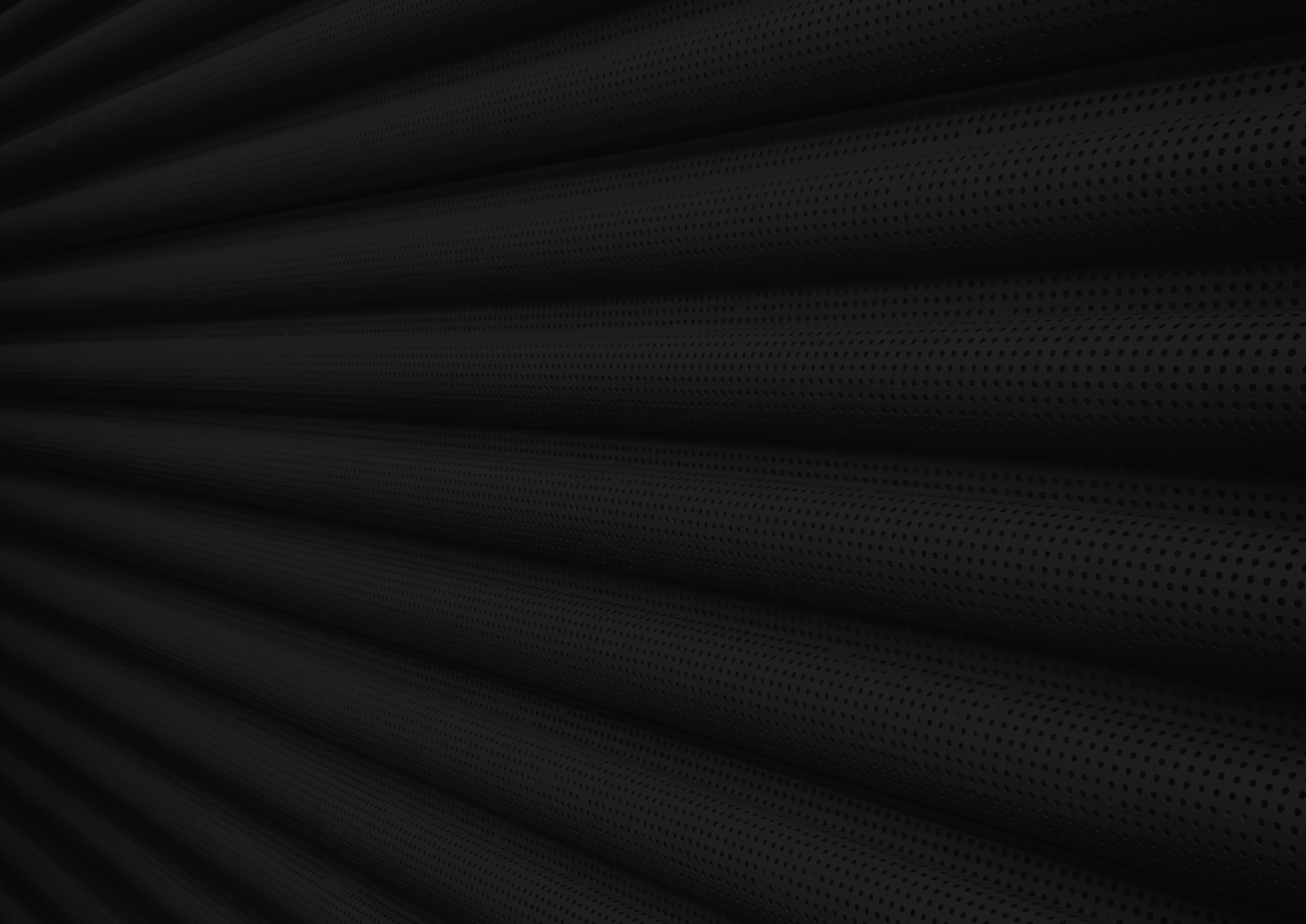
111. Zhang, G.; Zhang, T.; Lü, G.: Zhang, Y.; Liu, Y.; Zhang, W., 2016b. Effects of Microwave Roasting on the Kinetics of Extracting Vanadium from Vanadium Slag. JOM, 68(2), 577-584

112. Zhao, L.; Wang, L.; Qi, T.; Chen, D.; Zhao, H.; Liu, Y. 2014. A novel method to extract iron, titanium, vanadium, and chromium from high-chromium vanadium-bearing titanomagnetite concentrates. Hydrometallurgy 149, 106-109

113. Zhao, J.; Hu, Q.; Li, Y.; Liu, H. 2015. Efficient separation of vanadium from chromium by a novel ionic liquid-based synergistic extraction strategy. Chemical Engineering Journal 264, 487-496

114. Zhu, X.; Li, W.; Guan, X. 2016. Vanadium extraction from titano-magnetite by hydrofluoric acid. International Journal of Mineral Processing, 157, 55-59





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