A review of the vanadium primary production process chemistry

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A review of the chemical reactions involved in the vanadium primary production process was conducted. The conventional vanadium primary production process used in the industry involves Na_2CO_3-Na_2SO_4 roasting of titaniferous magnetite (titanomagnetite) feed concentrate with >1.4% V_2O_5 to produce a water-soluble sodium metavanadate ($NaVO_3$), leaching using water as lixiviant, desilication of the vanadium pregnant leach solution (PLS), precipitation of ammonium metavanadate (NH_4VO_3, AMV), and de-ammoniation and fusion to produce vanadium pentoxide (V_2O_5) flakes as a final or intermediate product. A feed with high contents of SiO_2, CaO, Al_2O_3, and Cr_2O_3 impurities results in chemical reactions with the sodium salt, resulting in excessive salt consumption and low vanadium extraction due to the formation of sparingly soluble calcium vanadates in water. Therefore roasting has to promote the chemical reactions to form sodium metavanadate and suppress the chemical reactions with impurities. If the roasting is ineffective, the leaching chemical reactions cannot be dictated to enhance the vanadium extraction and avert the dissolution of soluble impurity species like sodium silicate, without changing the lixiviant from water to the more corrosive and less selective acid and base solutions. The chemical reaction of aluminium sulfate and silicate ions in the pregnant leach solution (PLS) to precipitate aluminium silicate is an established desilication approach; however, it is not able to reject impurity chromium ions that might have dissolved from a high chromium-bearing titanomagnetite feed. AMV and de-ammoniation chemical reactions from a high-purity PLS are well established. However, the demand for even higher-purity vanadium products including vanadium electrolytes for vanadium redox flow batteries shows that there is a future for hydrometallurgical purification techniques such as solvent extraction and ion exchange for purifying the PLS to improve the vanadium primarily production process.

INTRODUCTION

Vanadium is a strategic metal that is primarily used as an additive to steel, in which it imparts important physical properties including high tensile strength, hardness, fatigue resistance, oxidation resistance, corrosive resistance, and radiation damage resistance (Project Blue, 2022; Gao, et al., 2021; Gilligan & Nikoloski, 2020). In 2022, approximately 93% of the global vanadium production was used for producing steel and other special alloys (Project Blue, 2022). Vanadium compounds have also been used in the chemicals industry from as early as the 1870s (Gupta & Krishnamurthy, 1992). Vanadium electrolyte is also used in energy storage systems in the form of vanadium redox flow batteries (VRFBs). It is projected that the vanadium demand for these applications will increase by approximately 3.7% per annum over the period to 2032.

Though the steel industry will continue to dominate vanadium consumption, it is forecast that the demand for VRFBs will account for a sizable portion of the growth of vanadium demand. Steel, alloys, and chemical industries will only experience modest consumption gains. The long-term rate of increase in vanadium demand in the energy sector is forecast to be even greater (Project Blue, 2022).

Titaniferous magnetite (titanomagnetite), with a crystal structure of $[Fe_2(Fe^{3+}, Ti^{3+}, V^{3+})_2O_4]$, is the primary source of vanadium throughout the world. Titanomagnetite deposits typically occur as magmatic accusations of ilmenite and magnetite, containing more than 1 mass% TiO_2 and 0.1 – 2 mass% V_2O_5. Though some vanadium occurs in ilmenite solid solution, it mainly occurs in the magnetite solid solution and the exsolved magmatic coulsonite (FeV_2O_4 or $FeO.V_2O_3$) endmember. There has been no report of discrete vanadium mineral phases in the prominent global titanomagnetite deposits (Yao & Mungall, 2022; Fischer, 1975).

Titanomagnetite accounted for about 87% of global vanadium production in 2022, with the remaining portion produced from secondary resources such as spent catalysts, uranium and alumina by-products, and ash derived from burning coal or petroleum. Titanomagnetite resources are found in many countries around the world, with the main commercialised resources found in China, Russia, South Africa, and Brazil. Industrial vanadium extraction from titanomagnetite is achieved through the steel and vanadium coproduction process or the vanadium primary production process. The coproduction process is an indirect vanadium production process, which typically involves titanomagnetite smelting to produce a titania slag by-product and a vanadium-bearing pig iron that is subsequently subjected to a converting process to produce steel and vanadium slag. The coproduction process is the main process used for extracting vanadium from titanomagnetite as it accounted for 70% of global vanadium production in 2022 (Project Blue, 2022). Coproduction operations are found in many countries around the world, including China, Russia, and South Africa (Steinberg, et al., 2011; Zhang, et al., 2007). In South Africa, the now-defunct EVRAZ Highveld Steel and Vanadium Corporation operated a coproduction plant (Steinberg, et al., 2011) and Ironveld Smelting (Bokone Smelting) commissioned a new coproduction operation in 2023 (Ironveld Group, 2023).

The alternative vanadium primary production process is essentially a roast-leach process. This process involves the roasting of titanomagnetite in the presence of sodium salt to convert vanadium in the titanomagnetite to the water-soluble sodium metavanadate ($NaVO_3$), leaching sodium metavanadate using water as lixiviant, precipitation of ammonium metavanadate (AMV, NH_4VO_3) from the pregnant leach solution (PLS), and de-ammoniation of AMV to produce the final or intermediate vanadium pentoxide (V_2O_5) product. The leach residue, referred to as calcine tailings or titaniferous leach residue, containing almost all the iron and titanium that were in the feed titanomagnetite, is discarded into waste dumps (Gao, et al., 2021; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Moskalyk & Alfantazi, 2003; Gupta & Krishnamurthy, 1992). The vanadium primary production process accounted for 17% of the global vanadium production in 2022, mainly from three operations around the world, i.e., Largo Resources in Brazil as well as Bushveld Minerals (Vametco and Vanchem operations) and Glencore (Rhovan operation) in South Africa (Project Blue, 2022; Gao, et al., 2021).

Though the coproduction process has higher vanadium throughput, the capital cost for the primary vanadium production process is significantly lower with better overall economics (Bushveld Minerals, 2014). As the vanadium demand is forecast to increase over the years to 2032, partly due to the projected commissioning of new VRFB production operations in China and other countries, the current vanadium production operations have to be optimised and new operations need to be developed to meet the forecast demand. New development projects for major vanadium production from titanomagnetite have been disclosed, namely, Australian Vanadium Limited (AVL) and Vanadium Resources (VR8) will be constructed and commissioned in Australia and South Africa, respectively. Both AVL and VR8 operations will be based on the lower-capital cost primary vanadium production process (Vanadium Resources, 2024; Australian Vanadium Limited, 2022). As is the case with the current primary vanadium producers, i.e., Bushveld Minerals, Glencore, and Largo Resources, the prospective vanadium primary producers will have a range of products such as vanadium pentoxide, vanadium trioxide (V_2O_3), ferrovanadium (FeV), nitro-vanadium (VN), and many other vanadium chemicals for use in a variety of industrial sectors. In these operations, vanadium pentoxide is an important product and precursor for producing other vanadium products, including the vanadium electrolyte for VRFBs.

The objective of this paper was to review the chemistry of the vanadium primary production process as it is applied in industry for the production of the vanadium pentoxide intermediate product, to provide a single and updated reference. The scope of work included the review of the conventional vanadium primary production process as implemented in different operations, and the opportunities for improving the process.

VANADIUM PRIMARY PRODUCTION PROCESS

Figure 1 presents the conventional vanadium primary production process flowsheet, including indicative vanadium extractions at respective process stages (Goso, et al., 2016). Although the details of the flowsheet vary from one operation to the other depending on different factors including the feed characteristics and era of commencement of the operation. (Gao, et al., 2021; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Moskalyk & Alfantazi, 2003; Gupta & Krishnamurthy, 1992).

As the objective of the work involves the review of the chemistry of the vanadium primary production process, physical separation techniques used to concentrate the run-of-mine titanomagnetite ore to produce a suitable feed for the chemical processes starting from the roasting stage, are not covered in the study. A mineral processing circuit involving crushing, milling, and magnetic separation is typically used to produce the titanomagnetite concentrate for the roasting stage of the vanadium primary production process (Connelly, 2024; Gilligan & Nikoloski, 2020; Moskalyk & Alfantazi, 2003).

The physical and chemical quality of the titanomagnetite concentrate is very important for the roasting and subsequent stages of the vanadium primary production process. The essential grind of the concentrate is based on the liberation of vanadium-bearing phases, mainly coulsonite, and to a lesser extent ilmenite, as determined by automated scanning electron microscopy (AutoSEM) techniques such as quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and mineral liberation analysis (MLA) (Connelly, 2024; Lv & Bai, 2019).

From a chemical point of view, the titanomagnetite feed must have low contents of impurities such as silica (SiO_2), alumina (Al_2O_3), lime (CaO), and chromium oxide (Cr_2O_3). The interferences presented by these species during the vanadium primary production process are described in the following subsections. Moreover, the V_2O_5 content in the titanomagnetite feed plays a significant role in determining the techno-economic feasibility of a vanadium primary production operation. Thus, the threshold of V_2O_5 content in the feed is also subject to economic factors and political circumstances prevailing in the country of the operation; for example, the costs of electricity, consumables, and labour. However, typical titanomagnetite feeds to the vanadium primary production process have more than 1.4% V_2O_5 content.

The chemical reactions involved in the respective stages of the vanadium primary production process are reviewed in the following subsections.

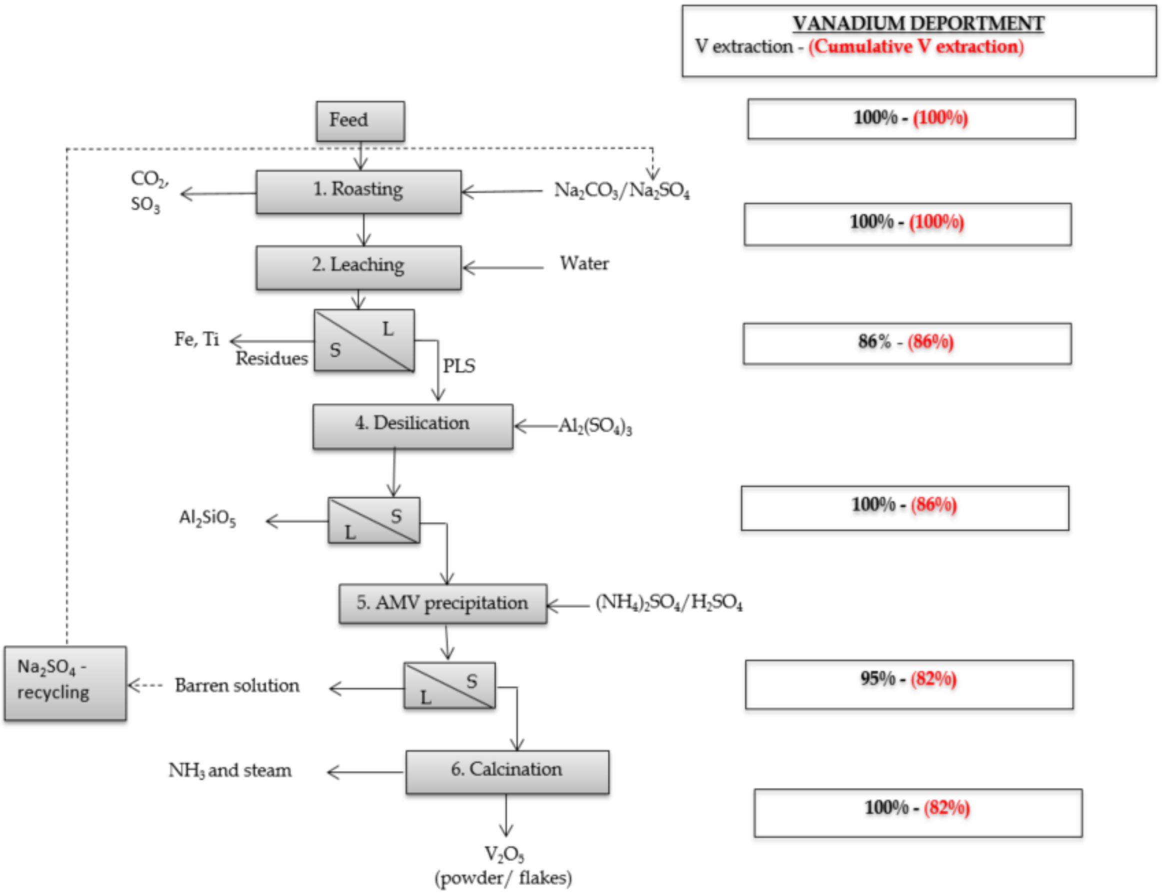

Figure 1. Generic vanadium primary production process flowsheet, adapted from Goso et al., *(2016).*

Roasting

The roasting of titanomagnetite concentrate is typically conducted using a rotary kiln. The objective of the roasting stage in the conventional vanadium primary production process is to convert vanadium in the titanomagnetite to a water-soluble sodium metavanadate ($NaVO_3$). Roasting is thus completed in the presence of a sodium salt. It is also important that the salt roasting is conducted under oxidising conditions with >4% free oxygen (Mefos, 2006). Salt roasting under oxidising conditions ensures the oxidation of magnetite to hematite to facilitate vanadium diffusion out of the magnetite lattice, thereby exposing it to oxidation from V^{3+}/V^{4+} minerals to V^{5+} compounds (Gilligan & Nikoloski, 2020; Mefos, 2006).

The reaction of vanadium in the titanomagnetite with typical sodium salts can be described using chemical reactions [1] to [3]. NaCl or chloride roasting is typically associated with low reagent cost and better vanadium reaction selectivity while operating at lower temperatures. However, it results in lower vanadium recoveries and the evolution of toxic HCl and Cl_2 gases that necessitate the use of special and expensive equipment resulting in higher capital costs and/or environmental and plant corrosion challenges (Gilligan & Nikoloski, 2020; Nkosi, et al., 2017; Taylor, et al., 2006; Moskalyk & Alfantazi, 2003; Gupta & Krishnamurthy, 1992).

Sulfate roasting also has high capital costs and environmental and corrosion challenges due to the emission of sulfur gas(es). It is also conducted at higher temperatures. However, in agreement with other literature (Mefos, 2006; Taylor, et al., 2006; Gupta & Krishnamurthy, 1992), Nkosi *et al.*, (2017) demonstrated that Na_2SO_4 roasting of a South African titanomagnetite concentrate resulted in higher vanadium extractions and better selectivity. Soda ash roasting is less selective for vanadium reaction in titanomagnetite as well as resulting in CO_2 emissions that adversely affect the environment.

$2NaCl_{(s)} + V_2O_{5(s)} + H_2O_{(l)} \rightarrow 2NaVO_{3(s)} + HCl_{(g)}$, chloride roasting at 800°C – 900°C [1]

$2NaCl_{(s)} + V_2O_{5(s)} \rightarrow 2NaVO_{3(s)} + Cl_{2(g)}$, chloride roasting at 800°C – 900°C [2]

$Na_2SO_{4(s)} + V_2O_{5(s)} \rightarrow 2NaVO_{3(s)} + SO_{3(g)}$, sulfate roasting at 1200°C – 1230°C [3]

$Na_2CO_{3(s)} + V_2O_{5(s)} \rightarrow 2NaVO_{3(s)} + CO_{2(s)}$, soda ash roasting at 900°C – 1200°C [4]

Industrial operations mainly use soda ash or Na_2CO_3 roasting as it has less complex environmental challenges (Connelly, 2024; Mefos, 2006). However, since Na_2SO_4 is readily recycled in the conventional vanadium primary production process, some Na_2CO_3 is replaced with Na_2SO_4 to achieve the combined benefits from a chemistry point of view. The mass ratio of Na_2CO_3: Na_2SO_4 used during roasting varies from one operation to the other. Overall, the use of recycled Na_2SO_4 lowers the amount of new Na_2CO_3 salt, which is one of the major contributors to the operational expenditure of the vanadium primary production process (Gilligan & Nikoloski, 2020; Hannam & Partners, 2023).

Some challenges to effective roasting

- High contents of impurities: A high content of silica in the feed would result in side reactions with the sodium salts according to the chemical reactions [5] and [6]. These reactions would result in wasteful salt consumption and contamination of the vanadium PLS produced from the leaching stage. To avoid excessive salt consumption, SiO_2 content in the feed titanomagnetite concentrate is kept below 3% SiO_2 (Connelly, 2024; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Mefos, 2006).

  $Na_2CO_{3(s)} + SiO_{2(s)} \rightarrow Na_2SiO_{3(s)} + CO_{2(g)}$ [5]

  $Na_2SO_{4(s)} + SiO_{2(s)} \rightarrow Na_2SiO_{3(s)} + SO_{3(g)}$ [6]

  The presence of alumina in the feed can also result in chemical reactions [7] and [8], assuming high activity of the Na_2O formed from the decomposition of the sodium salts. These reactions also result in high sodium salt consumption. At the typical roasting temperatures of up to 1250°C, it is unlikely that Al_2O_3 and SiO_2 would react to form stable mullite ($3Al_2O_3.2SiO_2$), sillimanite ($Al_2O_3.SiO_2$) and/or metakaolin ($Al_2O_3.2SiO_2$) such that the adverse effects of Al_2O_3 and SiO_2 in the feed are minimised. Connelly (2024) thus recommended that the combined contents of silica and alumina in the feed should be constrained below 4%. Otherwise, sodium salt consumption would be high and the contamination of the PLS would be severe, or there would be a rapid drop in vanadium recovery if the same salt addition is maintained for processing a feed with higher alumina and silica contents than 4%.

  $Na_2CO_{3(s)} + Al_2O_{3(s)} \rightarrow 2NaAlO_{2(s)} + CO_{2(g)}$ [7]

  $Na_2SO_{4(s)} + Al_2O_{3(s)} \rightarrow 2NaAlO_{2(s)} + SO_{3(g)}$ [8]

  High contents of chromium as free chromium oxide, magnesio-chromite, and chromite trigger reactions with the sodium salts resulting in the formation of water-soluble sodium chromate according to chemical reactions [9] to [14]. Thus, high chromium oxide content in the feed results in high sodium salt consumption and contamination of the vanadium PLS, subsequently necessitating a dedicated chromium rejection stage or causing the contamination of the final vanadium products (Gilligan & Nikoloski, 2020; Gupta & Krishnamurthy, 1992).

  $2Na_2CO_{3(s)} + Cr_2O_{3(s)} + 1.5O_2(g) \rightarrow 2Na_2CrO_{4(s)} + 2CO_{2(g)}$ [9]

  $2Na_2SO_{4(s)} + Cr_2O_{3(s)} + 2.5O_{2(g)} \rightarrow 2Na_2CrO_{4(s)} + 2SO_{3(g)}$ [10]

  $2Na_2CO_{3(s)} + MgCr_2O_{4(s)} + 1.5O_{2(g)} \rightarrow 2Na_2CrO_{4(s)} + MgO_{(s)} + 2CO_{2(g)}$ [11]

$$2Na_2SO_{4(s)} + MgCr_2O_{4(s)} + 2.5O_{2(g)} \rightarrow 2Na_2CrO_{4(s)} + MgO_{(s)} + 2SO_{3(g)} \qquad [12]$$

$$2Na_2CO_{3(s)} + FeCr_2O_{4(s)} + 1.75O_{2(g)} \rightarrow 2Na_2CrO_{4(s)} + 0.5Fe_2O_{3(s)} + 2CO_{2(g)} \qquad [13]$$

$$2Na_2SO_{4(s)} + FeCr_2O_{4(s)} + 1.75O_{2(g)} \rightarrow 2Na_2CrO_{4(s)} + 0.5Fe_2O_{3(s)} + 2SO_{3(g)} \qquad [14]$$

Free titania (TiO_2) present in the feed can also react with sodium salts according to the chemical reactions [15] and [16] (Gilligan & Nikoloski, 2020). When roasting titanomagnetite concentrate, these reactions are not reported to be a significant problem.

$$Na_2CO_{3(s)} + TiO_{2(s)} \rightarrow Na_2TiO_{3(s)} + CO_{2(g)} \qquad [15]$$

$$Na_2SO_{4(s)} + TiO_{2(s)} \rightarrow Na_2TiO_{3(s)} + SO_{3(g)} \qquad [16]$$

A high content of free lime in the feed causes the formation of insoluble vanadate through the chemical reaction [17], thereby compromising the vanadium extraction. Therefore the content of free lime in the titanomagnetite feed is limited to a maximum of 1% (Gilligan & Nikoloski, 2020; Goso, et al., 2016; Mefos, 2006). With excessive sodium salt in the roaster, the lost vanadium can however be recovered from the calcium vanadate through chemical reactions [18] and [19].

$$2CaO_{(s)} + 3V_2O_{5(s)} \rightarrow 2CaO.3V_2O_{5(s)} \qquad [17]$$

$$2CaO.3V_2O_{5(s)} + 3Na_2CO_{3(s)} \rightarrow 6NaVO_{3(s)} + 2CaO_{(s)} + 3CO_{2(g)} \qquad [18]$$

$$2CaO.3V_2O_{5(s)} + 3Na_2SO_{4(s)} \rightarrow 6NaVO_{3(s)} + 2CaO_{(s)} + 3SO_{3(g)} \qquad [19]$$

- Excessive or low stoichiometric Na_2CO_3 and Na_2SO_4 additions: Excessive addition of the sodium salt to the roasting process may, in addition to compromising selectivity by reacting with impurities in the feed, result in the formation of higher-order sodium vanadates, such as sodium orthovanadate (Na_3VO_4) or sodium pyrovanadate ($Na_2V_2O_7$). The formation of the higher-order sodium vanadates is shown in chemical reactions [20] to [23] (Gilligan & Nikoloski, 2020). Though the higher-order vanadates can be leached, their formation is unnecessary and costly as it requires more sodium salt additions.

$$3Na_2CO_{3(s)} + V_2O_{5(s)} \rightarrow 2Na_3VO_{4(s)} + 3CO_{2(s)} \qquad [20]$$

$$3Na_2SO_{4(s)} + V_2O_{5(s)} \rightarrow 2Na_3VO_{4(s)} + 3SO_{3(g)} \qquad [21]$$

$$2Na_2CO_{3(s)} + V_2O_{5(s)} \rightarrow Na_4V_2O_{7(s)} + 2CO_{2(s)} \qquad [22]$$

$$2Na_2SO_{4(s)} + V_2O_{5(s)} \rightarrow Na_4V_2O_{7(s)} + 2SO_{3(g)} \qquad [23]$$

In the case of insufficient sodium salt content in the roaster, the sparingly soluble sodium vanadate bronzes may form. Thus, impurities that react with the sodium salt in the feed need to be controlled and the necessary amount of sodium salt for conversion of vanadium should be added (Gilligan & Nikoloski, 2020).

- Excessive grinding of feed: As discussed above, titanomagnetite feed has to be ground to a suitable particle size necessary to liberate vanadium to facilitate roasting and leaching. However, if the feed is ground too much, it might be blown out of the rotary kiln during roasting (Gilligan & Nikoloski, 2020). Moreover, Goso *et al.*, (2016) showed that too finely ground titanomagnetite may result in low vanadium recoveries. This was attributed to sliming effects (Goso, et al., 2016).

The roasting stage of the vanadium primary production process is very important as it dictates the recoverable vanadium through the selective water-leaching process. If the roasting is ineffective, the leaching of vanadium cannot be improved downstream without changing the lixiviant from water to acid, thus increasing the cost of leaching reagents, compromising the selectivity of the process and complicating the vanadium purification and precipitation stages. More effort is generally placed on the roasting stage to ensure that the water-soluble $NaVO_3$ is effectively produced, with little or no presence of impurity species as described above.

Leaching

In industrial operations, the roast product or calcine from the kiln is typically quenched in water contained in a leaching tank. At Bushveld Minerals, the calcine from the kiln is fed into a wet ball mill for grinding for improved leaching, which forms the first of the three-stage leaching circuit (Hannam & Partners, 2023). The $NaVO_3$ formed during roasting using the sodium salts dissolves in water (Gilligan & Nikoloski, 2020; Taylor, et al., 2006; Gupta & Krishnamurthy, 1992; Rohrmann, 1985). The aqueous chemistry of vanadium is challenging since vanadium forms stable chemical species with oxidation states of 2 through 5. Above vanadium concentration of 0.001 M in a pH range of 3 – 13, vanadium ions polymerise into several chemical species including VO^{2+}, $V_2O_7^{4-}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$, $H_2VO_4^-$, $HV_4O_{12}^{3-}$, and HVO_4^{2-}. Figure 2 presents the Pourbaix diagram showing the stability ranges of vanadium chemical species in a 0.01 M vanadium solution at 25°C, produced in HSC Chemistry v7.1.1. Polyvanadates were not included in the presented Pourbaix diagram. Polyvanadates were included in the graphical representation of vanadium deportment in the pH range of 2 – 14 at 0.001 M V^{5+}, shown in Figure 3 (Gilligan & Nikoloski, 2020).

According to Figure 2 and Figure 3, around the neutral pH of water, i.e., solution pH of 6 – 8, the $NaVO_3$ contained in the calcine discharged from the kiln dissolves according to chemical reaction [24].

$$NaVO_{3(s)} + H_2O_{(l)} \rightarrow H_2VO_4^-{}_{(aq)} + Na^+{}_{(aq)} \qquad [24]$$

The figures also show that the dissolution of the higher order vanadates such as sodium pyrovanadate and orthovanadate may occur at high solution pH values of 8.5 and 13, respectively. The dissolutions of the sodium pyrovanadate and orthovanadate are presented by chemical reactions [25] and [26] (Gilligan & Nikoloski, 2020). Considering that industrial leaching is done using water as the lixiviant, the formation of sodium pyrovanadate and orthovanadate, through excessive sodium salt roasting, should be avoided as it may also complicate the leaching stage. In water, at pH 6 – 8, the dissolution of these higher-order vanadates and the overall vanadium extraction may be compromised.

$$Na_4V_2O_{7(s)} + H_2O_{(l)} \rightarrow 2HVO_4^{2-}{}_{(aq)} + 4Na^+{}_{(aq)} \qquad [25]$$

$$Na_3VO_{4(s)} \rightarrow VO_4^{3-}{}_{(aq)} + 3Na^+{}_{(aq)} \qquad [26]$$

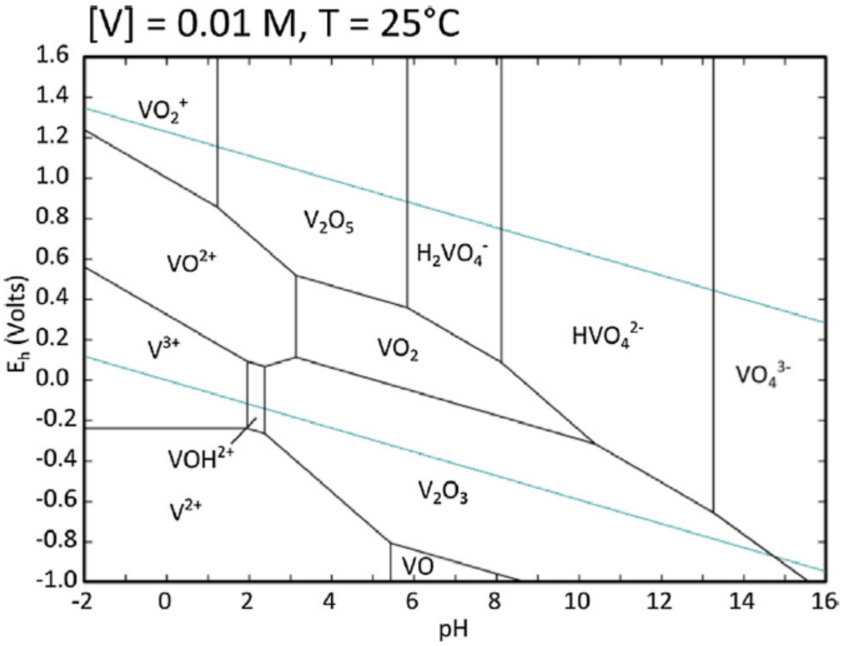

Figure 2. Pourbaix diagram showing the distribution of vanadium species in a 0.01 M vanadium solution at 25°C, produced in HSC Chemistry v7.1.1 (Gilligan & Nikoloski, 2020).

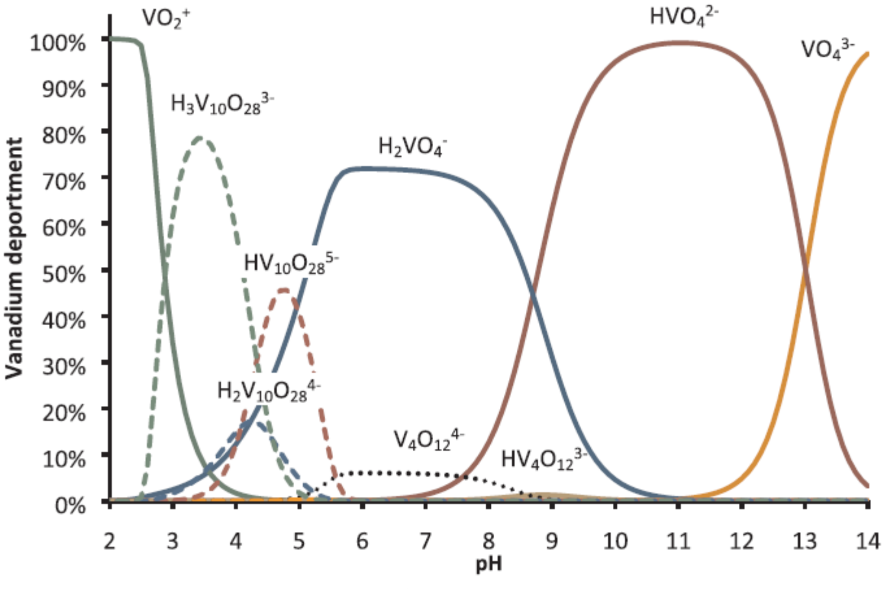

Figure 3. Vanadium deportment in the pH range of 2 – 14 at 0.001 M V^{5+}, produced with Visual Minteq v3.1. Between a pH of 4 and 9.5, the solubility of vanadium is less than 0.001 M, hence the total vanadium deportment is below 100% in this pH range (Gilligan & Nikoloski, 2020).

The impurity species such as Si, Al, Ca, Cr, and Ti contained in the calcine from the kiln may dissolve into the vanadium PLS. According to Gilligan and Nikoloski (2020), the dissolution of chromium species into the PLS may occur under strongly oxidising conditions or in a lixiviant with pH values of less than 2 or above 10. However, if Cr dissolves, it will follow vanadium and will subsequently contaminate the vanadium products, as the conventional vanadium primary production process does not have a dedicated stage to reject it. With the dissolution of Na_2TiO_3 species titanium dissolution may occur under strongly acidic conditions. In water or around neutral pH, only Na_2SiO_3, thus Si dissolves into the PLS (Gilligan & Nikoloski, 2020).

After several displacement washes of the calcine, the calcine tailings or leach solids are removed from the leaching dam and disposed of on the dedicated dump. The PLS, containing about 35 g/ L of vanadium from the leaching stage, is typically pumped to the thickeners where the desilication of vanadium takes place.

Desilication

The objective of this step is to remove silicon species from the PLS before the precipitation of AMV. High concentrations of silicon in the PLS typically result in the contamination of the high-purity vanadium products, which include the vanadium electrolyte used in VRFBs, FeV, and V_2O_5 used in chemicals and catalysis and that used to make specialty vanadium products like VN. The desilication process typically targets <0.05 g/ L of Si in the PLS before AMV precipitation.

In industry, the desilication of the vanadium PLS is typically done by adding sulfuric acid (H_2SO_4) to adjust the pH to 7.8 and aluminium sulfate [$Al_2(SO_4)_3$] to precipitate Si as aluminium silicate [$Al_2(SiO_3)_3$] (Connelly, 2024; Gilligan & Nikoloski, 2020). The desilication process may be presented as shown in the chemical reaction [27].

$$6Na^+_{(aq)} + 3SiO_3^{2-}{}_{(aq)} + Al_2(SO_4)_{3(s)} \rightarrow Al_2(SiO_3)_{3(s)} + 6Na^+_{(aq)} + 3SO_4^{2-}{}_{(aq)} \qquad [27]$$

AMV precipitation

In the vanadium primary production process, the high-purity vanadium PLS after desilication is typically subjected to precipitation. Industrial operations differ in the vanadium precipitate they produce. However, two vanadium precipitates, i.e., ammonium polyvanadate (APV) and AMV are generally produced (Connelly, 2024; Gao, et al., 2021; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Gupta & Krishnamurthy, 1992; Rohrmann, 1985). As shown in Figure 4, the target precipitate is mainly dictated by the solution pH, with APV precipitated when the solution pH ranges between 4 – 6 and AMV precipitated when the solution pH is 8 – 9. Due to the relative ease with which AMV is processed to produce V_2O_5 and other vanadium products, most industrial operations follow the AMV production route (Connelly, 2024; Hannam & Partners, 2023; Gao, et al., 2021).

AMV precipitation from the PLS made up of sodium metavanadate ions typically involves the adjustment of solution pH to about 8.4, followed by the addition of ammonium sulfate [$(NH_4)_2SO_4$] to produce ammonium metavanadate (NH_4VO_3) (Connelly, 2024; Gao, et al., 2021; Gilligan & Nikoloski, 2020; Goso, et al., 2016; Gupta & Krishnamurthy, 1992; Rohrmann, 1985). AMV precipitation process may be described by the chemical reaction [28].

$$2Na^+_{(aq)} + VO_3^{2-}{}_{(aq)} + NH_4SO_{4(s)} \rightarrow NH_4VO_{3(s)} + 2Na^+_{(aq)} + SO_4^{2-}{}_{(aq)} \qquad [28]$$

The sodium and sulfate ions remain in the barren solution, which typically contains < 0.56 g/ L V (or 1 g/ L V_2O_5) accounting for about 5% of the vanadium that was in the PLS. The barren solution is typically subjected to an evaporation process for the crystallisation of Na_2SO_4, which is the supplementary sodium salt to Na_2CO_3 used during the roasting stage. The crystallisation process may be described by the chemical reaction [29]. The recycled Na_2SO_4 allows for the roasting to be completed with a typical Na_2SO_4: Na_2CO_3 mass ratio of 15: 85. The condensate from the evaporation process after Na_2SO_4 recycling is availed for re-use as a lixiviant in the leaching stage.

$$2Na^+_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow Na_2SO_{4(s)} \qquad [29]$$

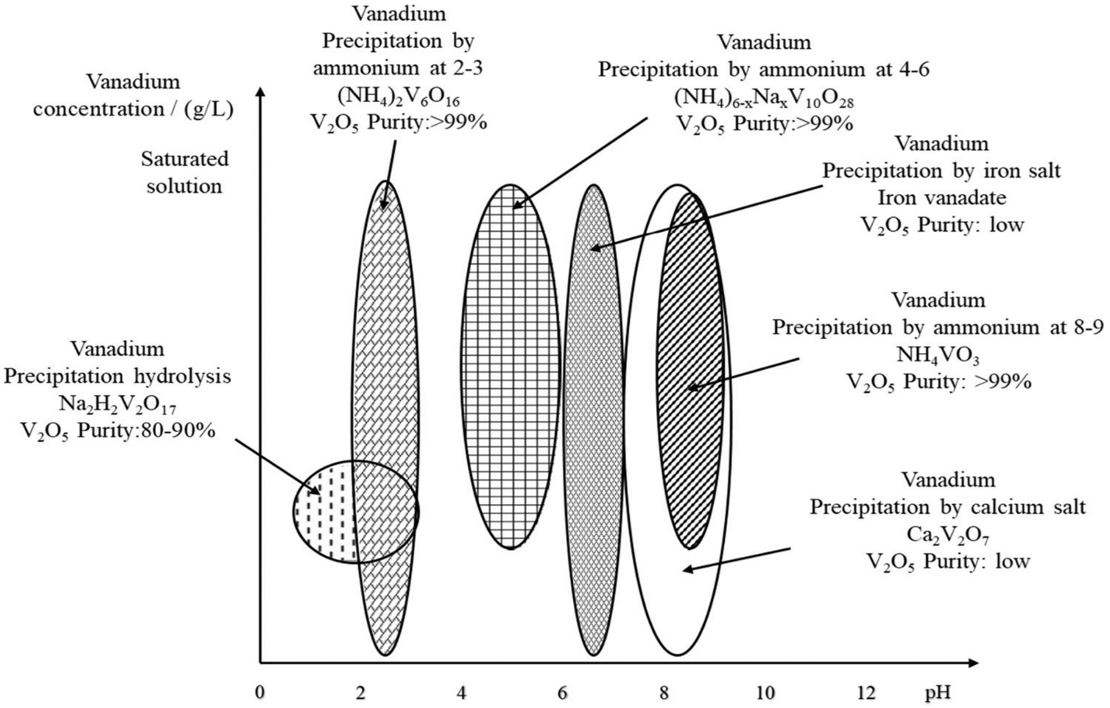

Figure 4. Graphical representation of the relationship between solution pH and the vanadium precipitate produced from a vanadium PLS (Gao, et al., 2021).

De-ammoniation, fusion, and flaking
The AMV cake is typically dried using a flash-dryer and subsequently calcined for de-ammoniation to produce V_2O_5 in a calciner. The thermal de-ammoniation of AMV may be described by the chemical reaction [30] (Hannam & Partners, 2023; Gao, et al., 2021; Gilligan & Nikoloski, 2020; Roskill, 2010; Rohrmann, 1985). The V_2O_5 is subsequently melted in a fusion furnace at a temperature of about 850°C, followed by continuous tapping onto a water-cooled flaking wheel. V_2O_5 solidifies and forms a thin layer on the rotating wheel. A metal blade positioned above the wheel scrapes off the solidified V_2O_5 from the wheel to produce the final product of V_2O_5 flakes (Hannam & Partners, 2023; Roskill, 2010; Rohrmann, 1985).

$$2NH_4VO_{3(s)} \rightarrow V_2O_{5(s)} + 2NH_{3(g)} + H_2O_{(g)} \qquad [30]$$

In integrated operations involving the production of FeV on-site or by a third party, the de-ammoniation process may be completed under a reducing atmosphere to produce V_2O_3. Less reductant is required during aluminothermic smelting of V_2O_3 for the production of FeV production, compared to when V_2O_5 is smelted. The de-ammoniation of AMV to produce V_2O_3 can be described by the chemical reaction [31] (Gilligan & Nikoloski, 2020).

$$2NH_4VO_{3(s)} + 2CO_{(g)} \rightarrow V_2O_{3(s)} + 2NH_{3(g)} + H_2O_{(g)} + 2CO_{2(g)} \qquad [31]$$

SOME OPPORTUNITIES TO IMPROVE THE VANADIUM PRIMARY PRODUCTION PROCESS

Valorisation of calcine tailings

Considering that the titanomagnetite concentrate fed to the vanadium primary production process in South Africa typically contains about 1.7% V_2O_5, 77.5% Fe_3O_4, and 12.5% TiO_2 (Goso, et al., 2016), the process thus results in the disposal of over 98% of the starting titanomagnetite concentrate as titaniferous leach residue or calcine tailings. The typical chemical composition of the calcine tailings produced in South Africa is shown in Table 1. The contents of TiO_2 and Fe_2O_3 have a combined total of about 90% of this by-product and make it attractive for valorisation for producing Fe and Ti products. In 2021, the overall size of the calcine tailings dumps was estimated to be more than 100 million tonnes (Gao, et al., 2021). Huge calcine tailings dumps are found in the countries that operate/operated the vanadium primary production process, including Australia, Brazil, and South Africa.

Table 1. Typical chemical composition of the titaniferous leach residue

SiO_2	Al_2O_3	K_2O	CaO	MgO	**TiO_2**	Na_2O	*V_2O_5	BaO	Cr_2O_3	**Fe_2O_3**	MnO	P_2O_5
2.36	3.69	0.01	0.14	1.27	**12.97**	1.30	0.46	0.02	0.43	**77.18**	0.28	0.02

*V_2O_5 content is more than the typical upper limit of 0.2 mass%, likely due to inadequate washing of tailings

The use of calcine tailings as feedstock in ironmaking furnaces is prohibited by several challenges, including the high sodium content that would severely attack the refractory lining of the furnace and the relatively low iron oxide content for economic ironmaking operations, especially electric arc furnaces (EAFs). The recent mothballing of the EHSV in South Africa, which operated a steel and vanadium coproduction process, is an indicator that it might not be economical to smelt the calcine tailings in EAFs for producing steel only. Successful valorisation of the calcine tailings would have a positive impact on the overall economics of the sodium salt-based vanadium primary production process, alleviation of environmental impact posed by the calcine tailings dumps, and the exploitation of valuable mineral resources for the economic growth in the operational countries.

Further purification of PLS

Production of vanadium products requires the precipitation of AMV from a high-purity PLS. More importantly, the increasing demand for vanadium in the energy storage sector requires the production of high-purity vanadium electrolytes. In addition to the Si impurity in the leach liquor, significant contents of Cr have been observed in some international titanomagnetites and have been observed in subsequent vanadium PLSs. Thus, further purification of the PLS is required to remove Cr, in addition to Si impurities to acceptable levels for downstream processing to produce the different vanadium products. Hydrometallurgical technologies such as solvent extraction and ion exchange may be explored for purifying the PLS to replace the precipitation-based desilication stage or used in conjunction with the standard desilication stage, particularly for the removal of Cr impurity species.

CONCLUSIONS

The review of the chemical reactions involved in the vanadium primary production process titanomagnetite showed that the roasting stage is very important as a pre-treatment stage to promote the chemical reactions to form sodium metavanadate and suppress the chemical reactions to form impurity species that would complicate the downstream process. If the roasting is ineffective, the leaching chemical reactions cannot be manipulated to enhance the vanadium extraction and avert the dissolution of soluble species like sodium silicate, without changing the lixiviant from water to the more corrosive and less selective acid and base solutions. Desilication is only capable of removing silicate impurities, and leaving behind impurity chromium ions that might have dissolved from a high chromium-bearing titanomagnetite feed.

The demand for higher-purity vanadium products including vanadium electrolytes for VRFBs presents an opportunity for the use of established purification techniques such as solvent extraction and ion exchange to purify the PLS for improving the robustness of the vanadium primarily production process. There exists another opportunity for improving the economics of the conventional primary production process through the development of technologies for the valorisation of historical and current calcine tailings.

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