VANADIUM AND ITS MAIN INDUSTRY: A REVIEW AND THE RESOURCE POTENTIAL IN CANADA

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Abstract

Vanadium is a strategic metal which is widely utilized in a variety of applications; (i) 63% in the production of high-quality metal alloys such as high-strength steel engineered for pipeline and commercial rebar applications (ii) 24% in the titanium-aluminum-vanadium alloys produced for the aerospace industry; and (iii) 13% in the chemical industry for the production of catalysts, electronics and batteries (e.g., vanadium redox batteries). New uses and applications are continually being discovered for this metal. Vanadium is relatively abundant in the Earth's crust,

but few primary economic deposits are known in the world. In 2018, China produced 54% of the world's vanadium, while the remainder of the global supply being derived from Russia (20%), South Africa (16%) and Brazil (10 %). Ninety-five percent of vanadium deposits worldwide are magmatic type deposits with the remaining 5% being sediment hosted deposits. The majority of the vanadium deposits in Canada are associated with layered mafic intrusions. Although there is substantial potential for vanadium in Canada, there currently exists no vanadium production or associated industry. Vanadium mineralization in Canada occurs in oxide-rich horizons within the layered gabbro zones of the upper parts of the Bell River Complex, Matagami, Quebec and the Doré Lake Complex, Chibougamau, Québec. There is also substantial vanadium potential in the Athabascan oil sands, Alberta, as well as Newfoundland and Labrador. Canada has the potential to become a large-scale vanadium producer especially with the wide variety of industrial applications situated in close proximity and elsewhere throughout North America. Therefore, it is recommended that Canada should seek to attract and develop robust new industries related to vanadium applications to make better use of its substantial vanadium potential.

1. Introduction

Vanadium (element 23 in the periodic table) was discovered twice: first in 1801 by the Spanish mineralogist Manuel del Rio at the School of Mines in Mexico City and then in 1830 at the School of Mines in Falun by the Swedish chemist Nils Sefström, who isolated it from an iron ore from the Taberg Mine in Sweden and called vanadium in honour of the Nordic goddess *Vanadis* because of the beautiful colors of its compounds. It was another Swedish chemist, Jöns Jacob Berzelius who later confirmed that both elements were one and the same. The metal was then isolated in powder form in England by Henry Roscoe in 1867 and was subsequently prepared in ductile form a few years later. However, it was not until 1903 that the first major application of the new metal started, and the vanadium industry expanded steadily through the 20th century and

continues to grow. The history of vanadium is reviewed by Habashi (2002), but this article is concerned with the future, exemplified by technological developments that imply continued demand for vanadium, and the presence of potential resources in Canada.

Vanadium is a strategic metal and has a variety of applications, primarily in the production of high-quality metal alloys, such as high-strength steel and titanium-aluminum-vanadium alloys. It has been predicted that the next generation of high-capacity wide-body jets will be built from vanadium-bearing titanium alloys (e.g. Ti-6Al-4V alloy). Vanadium foil has been proposed for use in superconducting cables, and vanadium alloys are under consideration for use in fusion applications. Finally, crystalline vanadium pentoxide is considered to be a key industrial material used in optical switches, chemical sensors, catalysts and solid-state batteries. It can be also manufactured into nanotubes that have many useful properties and potential applications. On the other hand, the steel industry is the largest consumer, accounting for 63% of usage, but specialized alloys used in the aerospace industry account for 24% of usage. Vanadium also has growing importance for the production of catalysts in the chemicals industry, electronics manufacture and in energy-storage applications such as vanadium redox batteries (Skyllas-Kazacos et al. 2016). The latter have attracted much attention in a world increasingly focused on clean energy. Non-alloy uses currently account for only 13% of usage, but they are expected to grow and new uses are continually being discovered for this metal. For a more detailed breakdown of vanadium usage and current trends, readers are referred to (Perles, 2014).

Vanadium is relatively abundant in the Earth's crust, but there are few primary economic deposits in which it is the main commodity; much vanadium production comes as a byproduct of other commodities, or from secondary industrial resources such as steel-industry slag. In 2018 (Polyak, 2018), China produced 54% of the world's vanadium, while the rest was split amongst Russia (20%), South Africa (16%), Brazil (10%) and others, including the United States, Japan, India, Korea, Australia and Taiwan. The total world production of vanadium in 2018 (Polyak, 2018) was about 80,000 tonnes, which is small compared to many other metals. However, world demand for vanadium is estimated to grow at a forecasted compound annual growth rate of 10.6% from 2013 to 2020 (Perles, 2014).

Vanadium is commonly associated with titanium (Ti), and most magmatic V deposits contain titanium and vice versa. The principal ore mineral in such deposits is titaniferous magnetite

containing vanadium. Primary magmatic deposits enriched in vanadium are spread around the world, mostly in South Africa, China, Russia and Canada (Figure 1) and these are all associated with layered mafic intrusions. Although magmatic deposits are the most important primary sources. Vanadium has been also found in deposits containing uranium, iron, and chromium, and also in bauxite deposits exploited for aluminum. As indicated in Table 1 (Habashi, 2002), vanadium is also enriched in bituminous deposits (e.g., oil sands and oil shales), and in coal, in phosphate deposits, in coal, oil, and graphite. The production of vanadium involves secondary sources such as steel-industry slag, and fly ash from power generation in addition to primary deposits of largely magmatic origin. This paper is focused on deposits of this type, with emphasis on some important examples in Quebec, Canada.

2. Vanadium Mineralization

Vanadium is relatively abundant in the Earth's crust as refractory metals. The relative abundance of the vanadium content of the earth's crust (Habashi, 2002) is 1.5×10^{-2} percent (=150 ppm) by mass, but few primary economic deposits (Figure 1) in which it is the main commodity are known or exploited. Vanadium mineralization is largely of magmatic origin, but there are examples of enrichment in sedimentary rocks, and these latter are increasingly important as exploration targets. Magmatic vanadium mineralization typically occurs in oxide-rich horizons within the upper parts of layered mafic intrusions such as the Bushveld Complex of South Africa (Willemse 1969; Von Gruenewaldt et al., 1985a and b; Reynolds 1985b; references therein). Although the Bushveld is widely considered as the type example for such deposits, and includes an important producer, many other mafic intrusions host such mineralization, including examples in Canada (Taner et al., 1998).

Figure 2 compares the overall stratigraphy of the Bushveld to layered intrusions in Quebec, Canada that are discussed in this paper. The distribution and geological relationships of these oxide-rich layers clearly indicate that they are of magmatic origin and that their genesis is directly related to processes that were operating during the late stages of fractional crystallization. Accordingly, the deposits are postulated to have formed by the accumulation of crystals of Fe-Ti oxide minerals via settling from an evolved melt (cf. Wager et al. 1960; Wager and Brown 1968; Irvine 1982; Guilbert and Park 1986) or by segregation and accumulation of a fluid rich in Fe and

Ti (Lister 1966; Lindsley 1991). Some workers (Maier et al., 1996) believe that physical processes within these dynamic magma chambers play an important role in concentrating the oxides, and that simple crystallization from magma cannot by itself account for oxide-rich zones.

Canada has substantial potential for economic deposits of vanadium associated with layered mafic intrusions of this general type, and the Doré Lake Complex at Chibougamau, Québec is the best know example (Allard 1976; Daigneault and Allard 1990). Vanadium in this area was discovered first in 1966 by G.O. Allard while working for the Quebec Department of Natural Resources, and at Bell River Complex at Matagami, Québec, was the site of a later discovery in 1997 by M.F. Taner (Taner and Allard 1998; Taner et al. 1998). The Matagami and Chibougamau mining districts (Figure 3) are located in the northern part of the Abitibi Subprovince, a large Archean greenstone belt, renowned for the abundance of Cu-Zn and Au deposits (cf. Franklin 1996; Lacroix 1998). These represent the main areas in Canada that have potential for vanadium production and are the main focus of this article.

Other examples of magmatic vanadium mineralization in Canada occurs at the Sept-Îles Complex, Québec (Cimon 1998; McCann 1998), the Lac St-Jean Anorthosite Suite, Québec (Mouksil et al. 2016), and the Pipestone Lake Anorthosite Complex, Manitoba (Jobin-Bevans et al. 1997). A recent review by Kerr et al. (2013) discussed vanadium potential in layered mafic intrusions and large anorthositic complexes in Labrador, but there is as yet no indication of significant resources in this area. Vanadium also occurs in association with some uranium deposits in Labrador (Kerr et al., 2013) and there is also interest in vanadium hosted in sedimentary rocks in several areas across Canada. Recent interest in potential resources, it is surprising that the most previous assessment across Canada was completed over 45 years ago (Rose, 1973). In this article, we summarize some of the developments that underlie increased interest in vanadium resources, and the main resources that are known to exist in Canada.

3. The Bell River Complex, Matagami Mining District, Quebec

The Bell River Complex is a large layered intrusion of Archean age (Freeman 1939; Jenney 1961; Sharp 1968; Scott 1980; Maier et al. 1996). The Complex played an important role as a heat source for the mineralization of a number of massive sulfide deposits in the Matagami mining district (Sharp 1968; Beaudry and Gaucher 1986; MacLean 1984; Piché et al. 1993). The regional

setting and local geology are summarized in Figure 3. The layered gabbro zone consists of distinctly layered Fe-Ti-oxide-rich gabbro, with associated leucogabbro, minor anorthosite and pyroxenite (Taner et al., 1998). Layering is well-defined by plagioclase-rich laminae (Figure 4) and a primary flow foliation is defined by oriented cumulus minerals, such as plagioclase and pyroxene. The widespread granophyric zone at the top of the complex contains quartz gabbro, diorite, granophyre and anorthositic gabbro. Vanadium mineralization in the Bell River Complex occurs within magnetite-and ilmenite-rich layers in the layered ferrogabbro zone of the upper part of the complex (Figure 2), and because of its high magnetic susceptibility it is easily detected as linear magnetic highs on magnetic geophysical survey maps (Figure 5). The classified inferred mineral resources, according to the National Instrument 43-101, were calculated by Dupéré (2011), using a minimum cut-off grade of 0.48% V_2O_5 and total 14,376,000 tonnes at 0.42% V_2O_5.

4. The Doré Lake Complex, Chibougamau Mining District, Quebec

The Doré Lake Complex is located about 250 km east of Matagami (Figure 3). It hosts many of the copper, silver and gold deposits in the Chibougamau mining district (Caty 1970; Allard 1976; Daigneault and Allard 1990; Girard and Allard 1998; Allard, 2002). According to Allard (1976), the ca. 2728 Ma Doré Lake Complex (DLC; 2728-2727 Ma) is a Bushveld-type layered intrusion. It is folded into a large anticline and metamorphosed to greenschist facies along with the enclosing volcanic rocks, with which it is coeval and co-magmatic. The Chibougamau district (Figure 7; Allard, 2002) is centered on the Chibougamau anticline flanked to the north by the Chibougamau syncline and to the south by the Chapais syncline. The district is best-known for copper and other base-metals, associated with volcanic and intrusive rocks, but there are also substantial resources of vanadium here. In fact, the Dore Lake Complex represents one of the largest undeveloped ferro-vanadium resources in the world. Two distinct Fe-Ti-V oxide horizons are identified on both limbs of the regional anticline (Figure 7). On the south limb, from bottom to top (Figure 2), the uppermost part the complex (Allard, 2002) is divided into the Anorthosite Zone (Main Zone), the Layered Zone, and Upper Border Zone (including the soda-granophyre and Ferrodiorite zones). The vanadium mineralization is contained in the lowermost part of the Layered Zone. The vanadium-rich zone consists of rhythmically layered units (50 to 200 metres-

thick layered zones) rich in ferroaugite, magnetite and ilmenite, intercalated with layers of leucogabbro. The Fe-Ti oxides at Doré Lake (Figure 6) are heterogeneously and rhythmically distributed, with Fe-Ti-oxide-rich horizons intercalated with oxide-free horizons. As a general rule, the vanadium content in magnetite decreases from base to top, a characteristic seen in other intrusions such as the Bushveld Igneous Complex (e.g., Guilbert and Park 1986). Conversely, the content of ilmenite (Fe-Ti oxide), both as free grains and in exsolution lamellae, increases from top to bottom in the sequence. On the south limb, Blackrock Metals Inc. reported measured and indicated resources of 240 million metric tonnes (Mt) at 37.8% Fe_2O_3, 7.0% TiO_2, and 0.42% V_2O_5.

5. Petrography of the Bell River and Dore Lake intrusions

The vanadium-bearing mineralization in the Bell River and Dore Lake intrusions is closely similar in many respects, and aspects of petrography, mineralogy and geochemistry are conveniently discussed together. Vanadium-bearing Fe-Ti-oxide zones (Taner et al., 1998) form specific layers in the upper parts of both the Bell River and Doré Lake layered complexes (Figure 2). Layering is sharply defined by 2 cm to 20 cm-thick leucocratic laminae (Figures 4 and 6), by bands of cumulus minerals (cf. Wager et al. 1960; Irvine 1982), or by discrete oxide-rich bands (Figures 4 and 6). In both complexes, the oxide-rich layers are concordant with the igneous layering of the host rocks. The continuity and lateral extent of these layers are well characterized by linear magnetic anomalies. In the Bell River Complex, the oxide-rich gabbro horizons are about 10 to 100 metres thick and have a subvertical attitude. The oxide-rich gabbro is a mineralized cumulate with disseminated oxide mineral contents of 20 to 60 modal % (Figure 4), or contains homogeneous, massive oxide bands, separated by oxide-poor gabbro. The massive bands have thicknesses of several centimetres to tens of centimetres, and oxide mineral contents of 50 to 90 modal % (Figure 6). These mineralized bands form 60-80% of the layered gabbro zone. There is a sharp contact between mineralized oxide-rich gabbro and host gabbro-anorthosite sequences in the Bell River Complex (Taner et al., 1998). A similar mode of occurrence (Figure 6) is also described for the Doré Lake Complex (Allard 1976; Girard and Allard 1998). Table 2 provides results of whole-rock analyses of mineralized oxide-rich gabbroic

units from both complexes, compared to data from the Bushveld Complex (from Willemse 1969; Von Gruenewaldt et al. 1985a and b; Reynolds 1985b and references therein).

6. Mineralogy

The main ore mineral for vanadium is magnetite (Fe_3O_4) but the actual vanadium content of magnetite is variable (Taner et al., 1998). This parameter is known as vanadium tenor, and is important in assessing any mineralization, as it represents the vanadium content of a magnetite-rich separate. Vanadium contents are typically reported as vanadium pentoxide (V_2O_5), but it is more likely that it occurs in trivalent form in magnetite, as it substitutes for iron (III). It is probably more correct to report vanadium contents as V_2O_3. The difference between these methods of presenting data are not large but are significant; 1% V_2O_3 would be about 1.2% V_2O_5, and both are substantially larger than when reported as the element, rather than an oxide. Such differences should be borne in mind when assessing data from individual projects.

Optical microscopy from complexes indicates that the oxide-rich mineralized zones in the Bell River and Dore Lake areas are medium-grained magnetite-ilmenite ferrogabbro (Taner et al., 1998). These rocks may be defined as mesocumulates to adcumulates according to the terminology of Wager et al. (1960). They consist of silicate minerals (30-80%), principally laths of plagioclase (1-3 mm in length) and subhedral elongated augite grains, along with interstitial Fe-Ti oxide minerals (20-70%). Rutile and titanite are dominant accessory minerals. The main oxide minerals are ilmenite and magnetite (Figures 7 and 8). They range in size from 1-2 mm to less than 5 μm, occurring as coarse- to medium-grained subhedral crystals intergrown with cumulus silicate minerals (plagioclase, pyroxene, etc.). The magnetite-ilmenite ratio ranges from about 1:1 to 2:1. As explained in detail below, most magnetite crystals contain tiny lamellae of ilmenite (Figure 9) that account for 20-40% of their volume.

Ilmenite, $FeTiO_3$, as titanium ore (Force 1991), occurs as separate grains 0.4-2 mm across and intergrown with titanian magnetite, which occupy interstices between cumulus minerals (Figures 7 and 8). The grains may occur alone or as aggregates that have smooth or irregular, sharp contacts with adjoining magnetite (Figure 8). A textural variety of the ilmenite occurs as exsolution laths with titaniferous magnetite (Figure 8) and, in some cases, constitutes irregular grains within magnetite. This lamellar textural variety was observed in both complexes (Taner et

al., 1998). Electron-microprobe analyses indicate that the ilmenite grains are compositionally homogeneous (Table 3). Small variations in Mn and Mg may be observed from sample to sample; for example, Mn is more abundant and Mg less abundant in Zone A-Matagami when compared to Zone B-Matagami (Taner et al., 1998).

Magnetite ($Fe^{2+}Fe^{3+}_2O_4$,) is the principal host for vanadium. Divalent iron may be replaced by Mg, Mn and, to a lesser, extent Ni or Zn, whereas the trivalent iron in magnetite may be replaced by Al, Ti, V and, more rarely by Cr. A number of exsolution products can be found in magnetite formed at high temperature, most commonly ilmenite, but also other spinels, including spinel *sensu stricto* ($MgAl_2O_4$), hercynite ($FeAl_2O_4$), and magnesioferrite ($MgFe_2O_4$). The ilmenite lamellae are well illustrated in Figure 9 (cf. Lister, 1966). The ilmenite lamellae vary in width, but this is not a continuous variation, as they are either wide or thin. The wider lamellae, which are 10 to 30 µm wide, are rare. The thinner lamellae are 1 to 3 µm wide (Figure 9) and lie within {111} octahedral crystallographic planes of the magnetite host. Thin sections cut parallel to {111} have a characteristic distribution of ilmenite laths in equilateral triangles forming a trellis texture. Trellis lamellae are generally attributed to "oxidation-exsolution", whereas other ilmenite exsolution textures can be products of either oxidation or primary crystallization (Buddington and Lindsley 1964; Haggerty 1991). Thin sections cut parallel to {100} planes in magnetite have ilmenite lamellae distributed in a square pattern (e.g., Figure 9). The wide lamellae are usually more widely spaced and continuous compared to the thinner lamellae that occur between them. The magnetite grain boundary with any adjoining grain of ilmenite is invariably very irregular (Figure 9).

 These textural relationships are well established in the literature, as illustrated by Ramdohr (1953, 1969) and Haggerty (1991). They have been reported for titaniferous magnetite from layered complexes such as the Bushveld Complex (Willemse 1969; Reynolds 1985a and b; Von Gruenewaldt et al. 1985a), the Duluth Complex (Lister 1966), the Sept-Îles Complex, Québec (Cimon 1998), the Pipestone Lake Anorthosite Complex, Manitoba (Jobin-Bevans et al. 1997), and the Skaergaard intrusion (Vincent and Philips 1954; Wager and Brown 1968).

There is a nomenclature problem in the literature because different varietal names have been used for macroscopically titanian magnetite that microscopically consists of intergrowths of ilmenite and magnetite. These names are *ilmenomagnetite* or *titaniferous magnetite* (Buddington and

Lindsley 1964), *titanomagnetite* (Ramdohr 1953, 1969; Von Gruenewaldt et al. 1985; Haggerty 1991), and *Ti magnetite* (Reynolds 1985a and b).

7. Vanadium Contents in Magnetite

Electron microprobe analyses of ore samples (Taner et al., 1998) from both types of complexes (Table 3) indicate that vanadium is more strongly partitioned into magnetite than ilmenite. The vanadium content of ilmenite grains is very low (the average value of 21 analyses is 0.18% equivalent V_2O_5), relative to magnetite samples (1.41% equivalent V_2O_5 (or 1.16% V_2O_3) for 20 analyses). This behavior is most likely due to the nearly identical ionic radius and charge of V^{3+} (0.64 Å) and Fe^{3+} (0.645 Å) (Shannon 1976). Consequently, magnetite, a mineral-rich in Fe^{3+}, would be expected to have higher V contents than ilmenite, a mineral poor in Fe^{3+}. The vanadium equivalent of magnetite is Coulsonite ($Fe^{2+}V^{3+}_2O_4$,) (Radtke 1962), found in titaniferous magnetite ores at Singhbum, India. Coulsonite represents the end member in $Fe^{3+} \rightarrow V^{3+}$ substitution in magnetite but is rare. On the other hand, geochemical behavior of vanadium in iron-titanium oxides was well studied by Schuiling and Freenstra (1980).

It is likely that the vanadium in magnetite is trivalent, not pentavalent. On the basis of both charge and size considerations, V^{5+} will not readily substitute for Fe^{2+}, yet it can substitute for Fe^{3+}. However, substitution of V^{5+} for Fe^{3+} introduces a charge imbalance in the magnetite structure that can only be offset by substitution of a small monovalent cation for Fe^{3+}, by means of a substitution mechanism like $2Fe^{3+} \leftrightarrow R^+ + V^{5+}$. The only suitable monovalent cation to play this role is Li^+ (0.76 Å, Shannon 1976) as all other monovalent cations are too large to stabilize the spinel structure. The plausibility of this substitution is supported by the synthetic spinel $CoLiV^{5+}O_4$ (Gonzalez et al. 1996). However, mafic magmas are so notoriously impoverished in Li that discussions regarding V^{5+} are moot.

Routine beneficiation of vanadium ores results in an oxidized product hence the reporting of refined vanadium ore concentrates is commonly in wt.% V_2O_5. This has led most previous researchers to erroneously report vanadium concentrations of unrefined magnetite-bearing ore and ore minerals in wt.% V_2O_5 (e.g., Klemm et al. 1985; Reynolds 1985b; Von Gruenewaldt et al. 1985a). For scientific accuracy, analyses of unrefined vanadian magnetite ore and ore minerals really should be reported in wt.% V_2O_3. This is certainly a necessity when using analyses of

ilmenite-magnetite pairs for geothermometry (e.g., Stormer 1983). Nonetheless, we advocate supplementing analytical results with *equivalent* V_2O_5 (= $V_2O_3 \times 1.2135$), for a tie to previously published data and to provide a measure of vanadium concentration preferred by industry (cf. Tables 2 and 3).

8. Ore Beneficiation

The presence of vanadium in magnetite from oxide-rich rocks in layered intrusions is not by itself an indication of commercial viability. This aspect of vanadium deposits is critically dependent upon mineralogical details, and especially on grain size and the nature of mineral intergrowths. Several recent technological advances have had a positive effect on the profitability of vanadium projects. For example, advances in Wet High Intensity Magnetic Separation (WHIMS) technologies have led to substantial improvements in vanadium recovery. The mineralogical data (Taner et al., 1998) from the Bell River and Dore Lake areas is very important in the development of a commercial extraction procedure for vanadium.

According to Taner et al. (1998), the main vanadium-bearing mineral in both complexes is magnetite. These vanadium ores also contain economic quantities of ilmenite, as a titanium ore. Accordingly, the proposed processing method has multiple steps: (1) Grinding of the ore to an average grain-size of 40-50 μm, for a good initial degree of liberation; (2) Gravimetric separation of oxide ore minerals (ilmenite and magnetite) from silicate gangue minerals (plagioclase, pyroxene, chlorite, etc.), resulting in a medium-grade V-Ti ore and an environmentally safe waste; (3) Concentration of vanadium ore (magnetite) by magnetic separation and of titanium ore (ilmenite) by flotation. Because of the extremely fine scale of the ilmenite lamellae in the magnetite, it is not practical to attempt physical separation of the intergrowths; (4) Application of a vanadium-extraction process on the vanadium ore, which will inevitably still contain some titanium (Hukkanen and Walden 1985).

9. Production of Vanadium Pentoxide

Vanadium pentoxide has been produced from vanadiferous magnetite for over 30 years using the classic sodium salt roasting process (Bradbury, 2002). Some processing plants utilize vanadium-rich slags derived from steel production whereas some smaller scale producers also utilize oil residues and spent catalyst as vanadium sources (feedstock). Various other techniques to extract the vanadium have been tried over the years, including pressure leach, acid and caustic digestion. However, none of these processes have yet proven to be as cost effective as the sodium roast. Bradbury (2002), succinctly provides an overview of current operating practice and some of the process developments that have taken place in the sodium salt roast process for the production of vanadium pentoxide. The challenges that the modern producer faces, especially with respect to environmental issues and cost reduction, are highlighted. The production of purified vanadium solutions, suitable for vanadium battery electrolyte is also discussed. Monskalyk and Alfantazi (2003), also gave a nice review of vanadium processing.

## 10. Electrochemical Energy Storage Systems and Application

The largest commercial application for vanadium in energy storage is in its use as the electrolyte for the All-Vanadium Redox Flow Battery (VFB) (Figure 10). The VFB was first invented in the mid-1980s by Skyllas-Kazacos and coworkers at the University of New South Wales (UNSW Sydney) Australia (Skyllas-Kazacos et al. 1986; Skyllas-Kazacos and Robins 1988), and while it saw significant field testing in Japan during the 1990s, it was not until the basic patent expired in 2006 that commercialization expanded around the world (Skyllas-Kazacos et al. 2011).

Like all other types of flow batteries, the VFB uses two solutions in external tanks to store energy (Figure 11). These solutions are pumped through a series of cells (a cell stack) where electron transfer reactions take place at inert electrodes, thereby generating electrical energy. Inside the cell stack, ion exchange membranes separate the two half-cell solutions, but diffusion of ions across the membrane can lead to loss of capacity and cross-contamination of the solutions. This problem was solved by Skyllas-Kazacos and co-workers by using the same element in both half-cells (Skyllas-Kazacos and Robins 1988). Vanadium is known to exist in several oxidation states, elemental V, V(II), V(III), V(IV) and V(V), but the low solubility of V(V) compounds had previously ruled out the use of the V(IV)/V(V) redox couple in a flow battery application. Skyllas-Kazacos's group found that by electrochemically oxidizing a concentrated $VOSO_4$

solution, V(V) concentrations of 2 M could be readily generated, allowing the development of a practical All-Vanadium Redox Flow Battery that employed the V(II)/V(III) and V(IV)/V(V) couples in the negative and positive half-cells respectively. The high cost of $VOSO_4$ precluded its use as the raw material for the VFB electrolyte, so Skyllas-Kazacos and co-workers developed a number of processes to chemically or electrolytically reduce V_2O_5 to produce a 50:50 mixture of V(III) and V(IV) (referred to as $V^{3.5+}$) that could then be used as the starting electrolyte in both half-cells (Skyllas-Kazacos et al. 1988). The initial charging and subsequent charge-discharge reactions of the VFB are as follows:
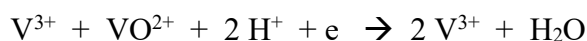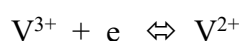
Positive half-cell cell:

Initial charging reaction:

$$V^{3+} + VO^{2+} + H_2O \rightarrow 2\ VO^{2+} + 2\ H^+ + e$$

Subsequent charge-discharge reaction:

$$VO^{2+} + H_2O \Leftrightarrow VO_2^+ + 2\ H^+ + e$$
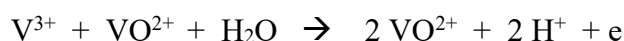
 Negative half-cell:

Initial charging reaction:

$$V^{3+} + VO^{2+} + 2\ H^+ + e \rightarrow 2\ V^{3+} + H_2O$$

Subsequent charge-discharge reaction:

$$V^{3+} + e \Leftrightarrow V^{2+}$$

Overall cell reaction:

$$VO^{2+} + V^{3+} + H_2O \Leftrightarrow VO_2^+ + V^{2+} + 2\ H^+$$

The overall cell reaction has a standard reduction potential of 1.26V, but for a typical 2 M vanadium electrolyte, the open-circuit potential is 1.4 V at 50% state-of-charge. The total vanadium ion concentration used in practical systems determines the energy density of the VFB and this is set by the saturation solubility of each of the vanadium ions in the sulphuric acid supporting electrolyte within the desired temperature range (Skyllas-Kazacos et al. 2016). As illustrated in Figure 12, the solubility of V(II), V(III) and V(IV) sulphates in sulphuric acid increases with temperature but decreases with increasing sulphuric acid concentration due to the

common ion effect of the sulphate species in solution. On the other hand, however, V(V) undergoes an endothermic thermal precipitation reaction to V_2O_5, so its solubility decreases with increasing temperature and decreasing acid concentration in accordance with the following equilibrium reaction:

$$2\ VO_2^+\ +\ H_2O\ \Leftrightarrow\ V_2O_5\ +\ 2\ H^+$$
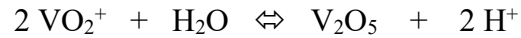
Because of these solubility trends, practical VFB electrolyte compositions are usually in the range 1.6 to 2 M vanadium in 4 to 5 M sulphuric acid/total sulphate, while the operating temperature range is between 10 and 40°C. In order to suppress the vanadium ion precipitation reactions and allow cell operation over an extended temperature range and higher vanadium ion concentrations, in the mid-1990s, Skyllas-Kazacos and coworkers proposed the use of stabilising additives or precipitation inhibitors (Skyllas-Kazacos 1996; Skyllas-Kazacos and Kazacos 2000; Mousa and Skyllas-Kazacos 2015; Roe et al. 2015; Kausar et al. 2015). A wide range of additives and additive combinations was found to successfully stabilise each of the vanadium ions at concentrations up to 3 M and temperatures between 5°C and 50°C, by increasing the induction time for precipitation.

During the 1990s, the UNSW group also conducted extensive research and development of all aspects of the VFB including electrolyte chemistry and production, electrodes and electrode modification (Skyllas-Kazacos et al. 2011; Ulaganathan et al. 2016), membrane selection and optimisation (Prifti et al. 2012), cell and stack design, sensors, battery control systems, mathematical modelling and simulation (Skyllas-Kazacos and McCann 2014). They also installed a VFB in a solar demonstration house in Thailand and carried out field tests with a VRB powered electric golf cart (Skyllas-Kazacos and McCann 2014). In the mid-1990s, UNSW licensed the technology to Mitsubishi Chemicals and Kashima-Kita Electric Power Corporation who subsequently conducted field trials of a 200 kW/800 kWh VFB in a load-levelling application at one of their power stations in Japan, before transferring their licence and technology to Sumitomo Electric Industries. During the late 1990s and early 2000s, Sumitomo successfully demonstrated the VFB technology in a wide range of applications including solar and wind storage, peak shaving, emergency back-up power, frequency regulation and voltage sag protection, while also achieving long cycle life of more than 200,000 cycles in a wind energy field trial in Japan,

In 2015, a 30 kW/130 kWh commercial VFB system was installed in the Tyree Building at UNSW Sydney by the German company Gildemeister (Figure 13). The system is connected to the building grid and to a 140 kW PV array on the roof. Several companies are now commercially producing and installing VFB systems based in the original UNSW technology. These include Sumitomo (Japan), Rongke Power (China), RedT (UK) and Schmid Energy (Germany). In 2016, Rongke Power announced approval to install a 200 MW/800 MWh VFB system in Dalian China. Construction began in October 2016 and after full commissioning, the VFB battery will be able to peak-shave approximately 8% of Dalian's expected load in 2020. In addition, battery will enhance grid stabilization including securing power supply and providing black-start capabilities in the event of emergencies.

In 2012, researchers at Pacific Northwest National Laboratories (Wang et al. 2012), reported an improved VFB electrolyte involving the use of a sulphuric acid/HCl mixture as the supporting electrolyte. By adding HCl to the standard sulphuric acid electrolyte, the increased proton concentration is able to enhance the solubility of the V(V) species, without increasing the total sulphate concentration that adversely affects the solubility of the V(II), V(III) and V(IV) species. This mixed acid electrolyte allows operation with 2.2 M vanadium electrolytes and a wider operating temperature range of 0 to 50°C. This mixed acid electrolyte technology was licensed to UniEnergy Technologies (UET) and is currently being commercialised in the USA.

11. Discussion and Conclusions

Vanadium is a strategic metal that has many important industrial applications, largely in producing high-quality specialized metal alloys and strengthened steel. Currently, its uses in the chemical industry and in energy applications are subordinate, but their future is of much interest. The vanadium industry is only about 60 years old and new uses are continually being discovered for the metal (Table 4). Vanadium foil is used as a bonding agent in cladding titanium to steel and generally by the aerospace industry. Medical implants commonly contain vanadium alloys because of their excellent stability. Some vanadium compounds are used as catalysts in chemical processes such as the production of sulfuric acid. The vanadium redox flow battery (VFB) is the development that has attracted most attention. The VFB is thought to have potential in load leveling within electrical systems, in providing back-up power sources, and crucially for storage

of electricity from wind and solar power. These 'renewable' energy sources currently lack large-scale capacity for storage of the energy that they produce.

There are new markets for vanadium, developing as a consequence of new applications. The development of most interest is the new vanadium redox battery, which is currently being commercialized in Japan, UK, Korea, China, Germany, USA and Australia for large-scale energy storage applications and potentially in electric vehicles. There is also growth in the use of vanadium in catalytic applications. The material possesses an outstanding structural versatility and can be manufactured into nanotubes that have many useful properties and potential applications. The energy storage industry has the greatest potential to increase demand. With vanadium requirements of over 6 kg V_2O_5 per kWh of installed capacity, the 800 MWh VFB installation in China will require more than 4,800 tonnes of vanadium pentoxide, highlighting the potential for market growth.

The main vanadium products, traded internationally, or entering international trade are: (a) vanadium-bearing slags and ores; (b) ashes, residues and spent catalysts; (c) vanadiferous pig iron; (d) vanadium pentoxide; (e) ferrovanadium; (f) wrought and unwrought vanadium metal; (g) vanadium metal waste and scrap; and (h) other oxides and hydroxides. According to Byron Capital Markets (Hykawy, 2009), the potential vanadium supply between 2010 to 2014 is about 67,200 t (2010), 72,500 t (2011), 76,000 t (2012), 89,000 t (2013) and 89,000 t (2014), and vanadium demand is about 61,128 t (2010), 69,390 t (2011), 76,520 t (2012), 85,093 t (2013) and 96,094 t (2014).

In view of these developments, there is a future substantial potential for developing primary vanadium resources that are known in Canada. Most of these vanadium deposits are associated with layered mafic intrusions, although potential also exists for sediment-hosted deposit types, including black shales, and also for by product extraction from oil sands and oil shales.

Amongst the vanadium deposits that are defined in Canada, the resources in the Bell River and Dore Lake complexes are the best known and most developed. However, they are by no means the only mafic intrusions that may have potential to host important resources. There remains much scope for research in these areas, in conjunction with ongoing exploration, but also for fundamental investigations of other mafic intrusions.

Acknowledgments

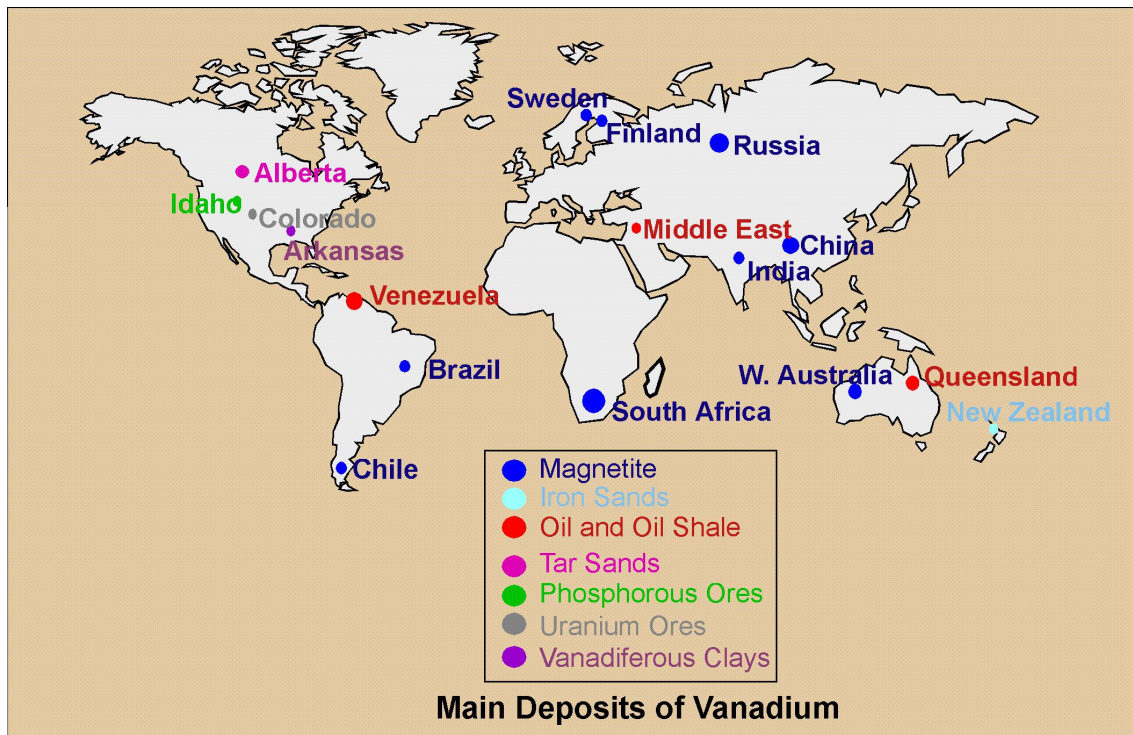# Figures and Tables

Figures

Figure 1. Main vanadium deposits in the world (Modified from Gupta and Krishnammurthy, 1992).
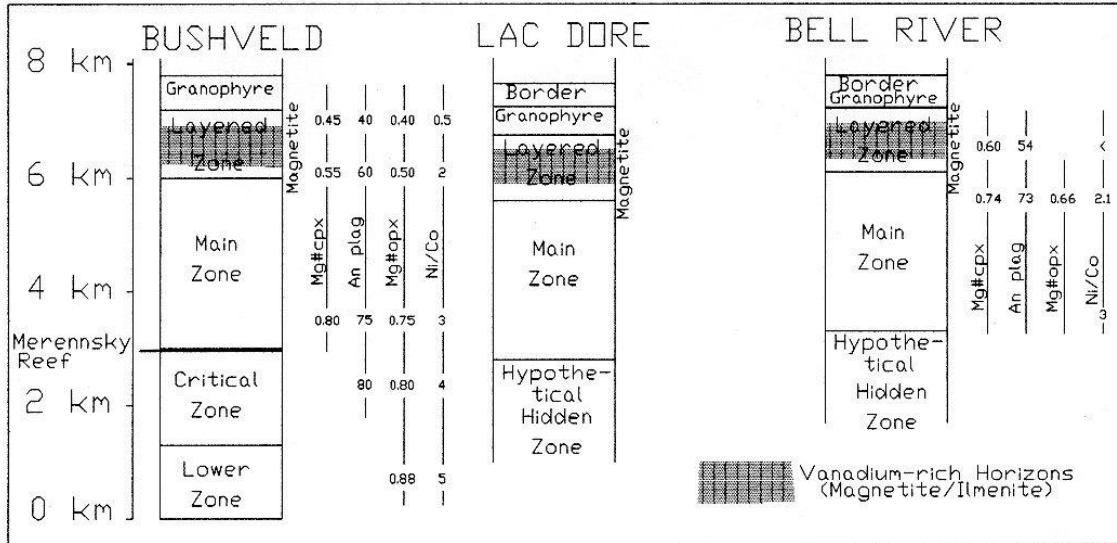
Figure 2. Comparison of the Schematic Stratigraphic Column, Mineral Chemistry and Ni/Co ratio of the Bushveld, Lac Dore and Bell River layered complexes (modified from Maier et al.,1996)
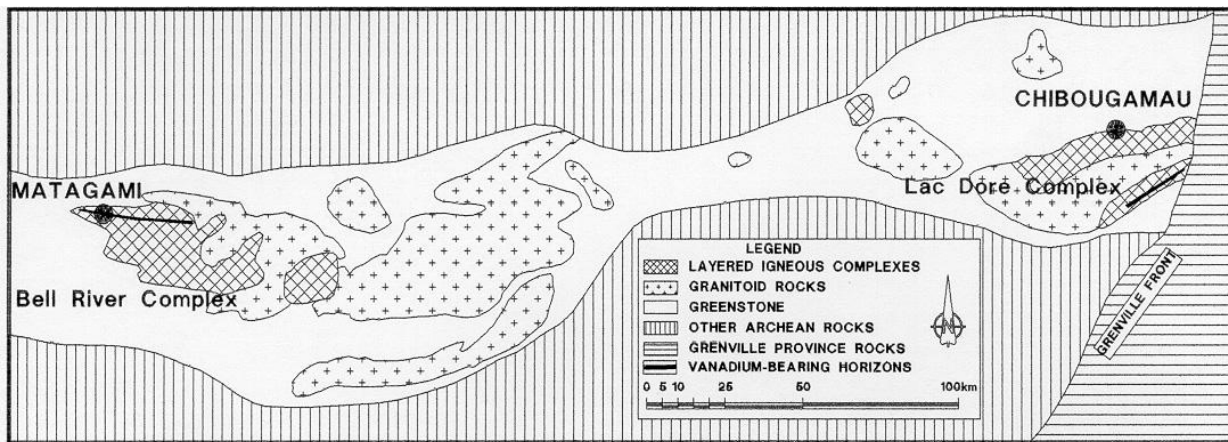

Figure 3. Simplified Geological Map of the Matagami-Chibougamau area, the Northern part of the Abitibi Greenstone Belt, Quebec (modified from MacLean, 1984)

Figures 4a and b. Typical outcrops of vanadium-bearing oxide-rich gabbroic rocks from the Bell River complex, showing mineralized bands that host 50-90% magnetite + ilmenite and form 80% of the whole layered gabbroic unit.
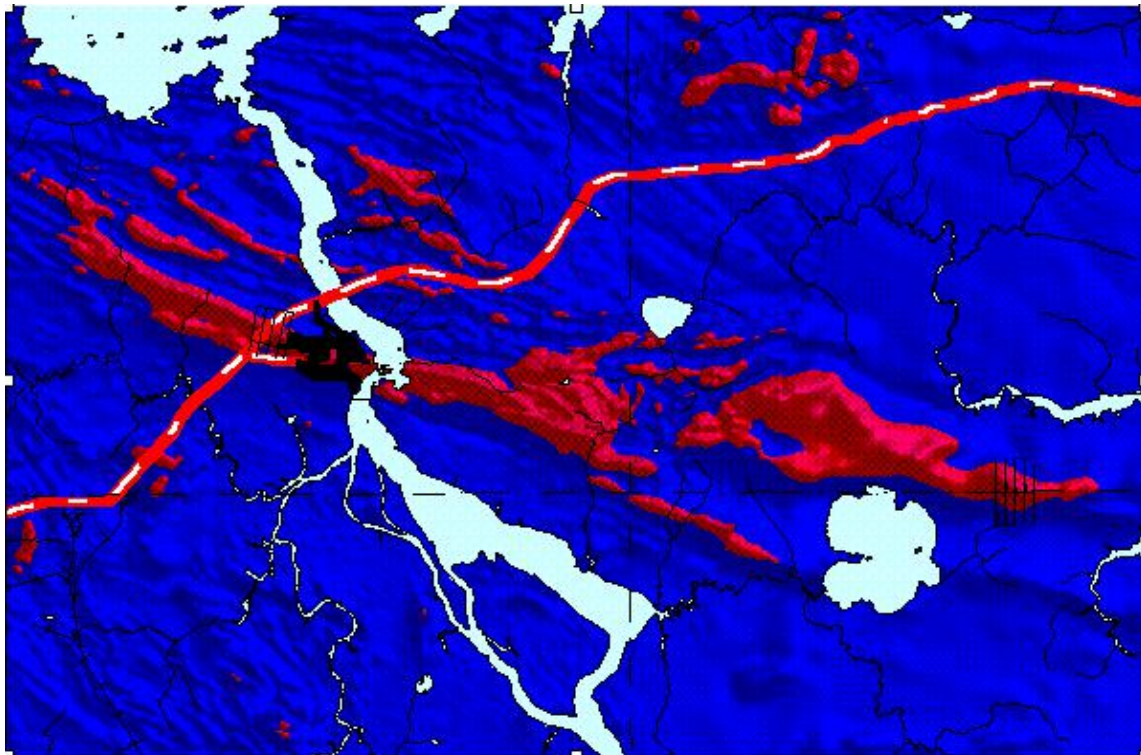

Figure 5. Matagami Fe-Ti-V deposit: Magnetic map, interpreted from aeromagnetic data by M. Allard (Taner and Allard,1998).

Figures 6a and b. Typical outcrops of vanadium-bearing oxide-rich gabbroic rocks from the Dore Lake complex (on Rinfret Tp.), showing rhythmic layering with magnetite-ilmenite rich horizons (scale: camera lens cover = 5 cm diameter)
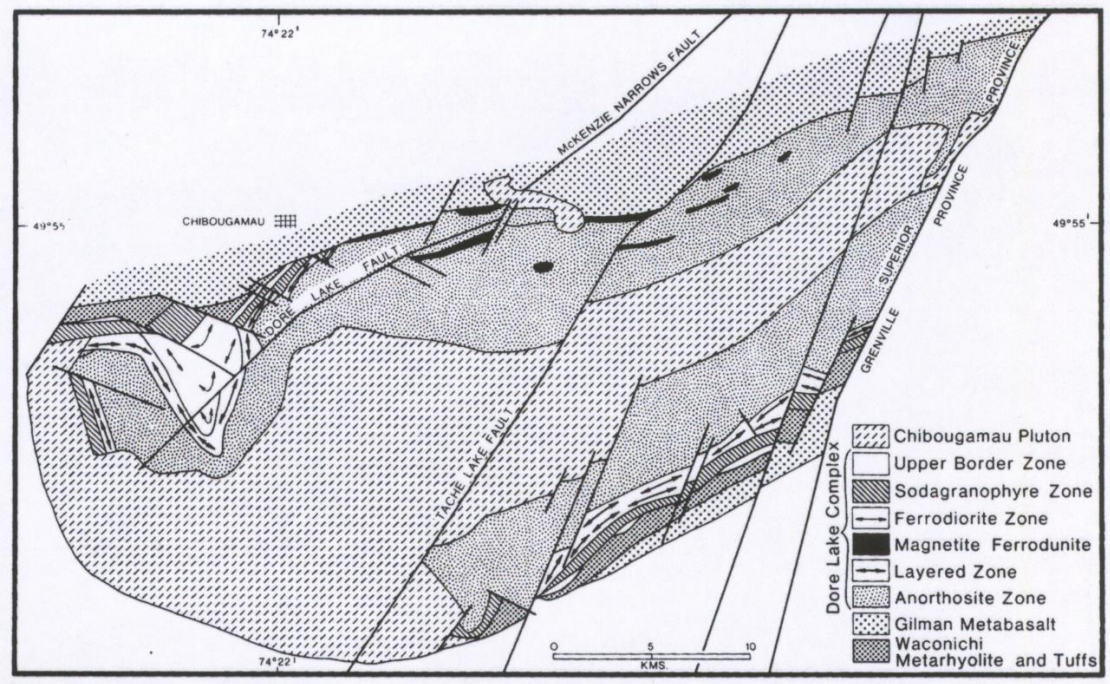

Figure 7. Geological sketch map of the Chibougamau district (modified from Allard, 2002).

Figure 8. Photomicrograph of vanadium-rich sample from the Bell River Complex (Taner et al., 1998). This photo shows the relationship between cumulus silicate minerals and interstitial oxide minerals (medium gray magnetite and light grey ilmenite: reflected light, 1.8 mm field of view).
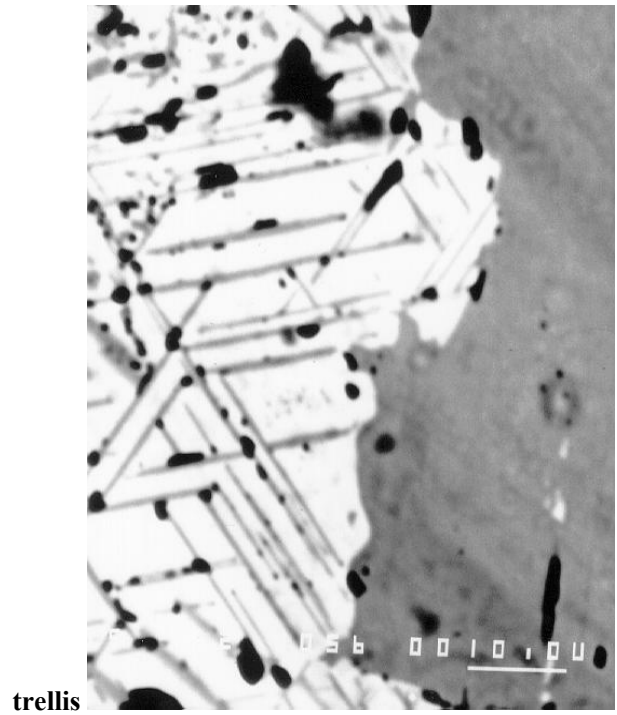
trellis

Figure 9. Backscattered-electron microprobe image of vanadium-rich sample from the Bell River Complex (Taner et al., 1998) showing the homogeneous ilmenite grain and the vanadium-bearing ilmeno-magnetite with trellis-textured ilmenite (section subparallel to $\{111\}_{magnetite}$; scale bar =10μm)
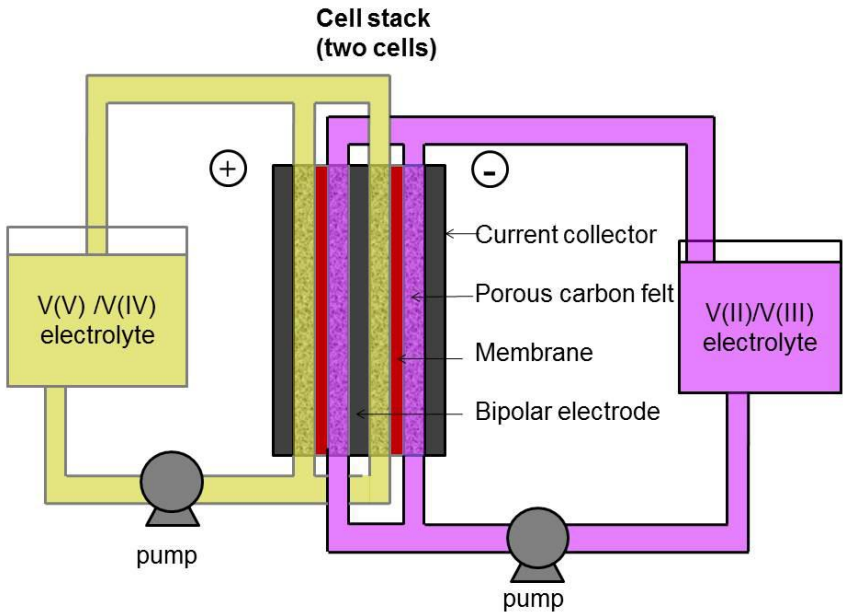

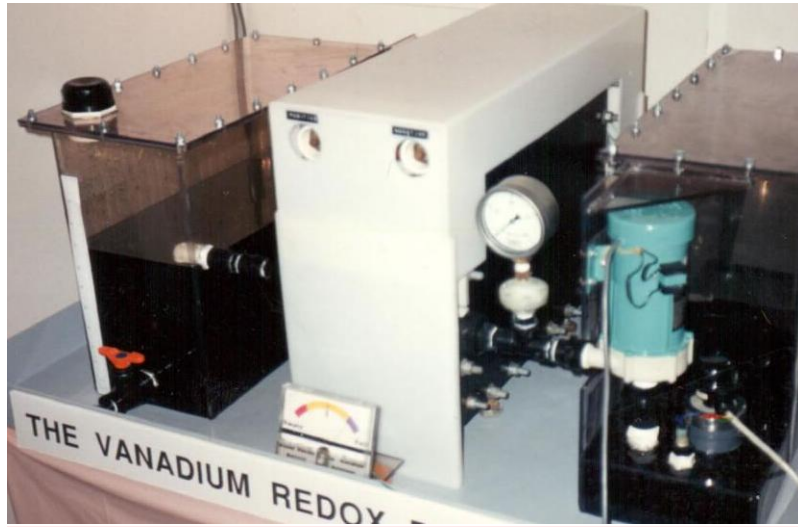**Figure 10. Simplified schema of vanadium redox battery**

Figure 11. Early 1 kW VFB Prototype at UNSW Sydney (approximately 1990) showing battery stack and electrolyte tanks for the V(II)/V(III) negative and V(IV)/V(V) positive half-cell electrolytes.
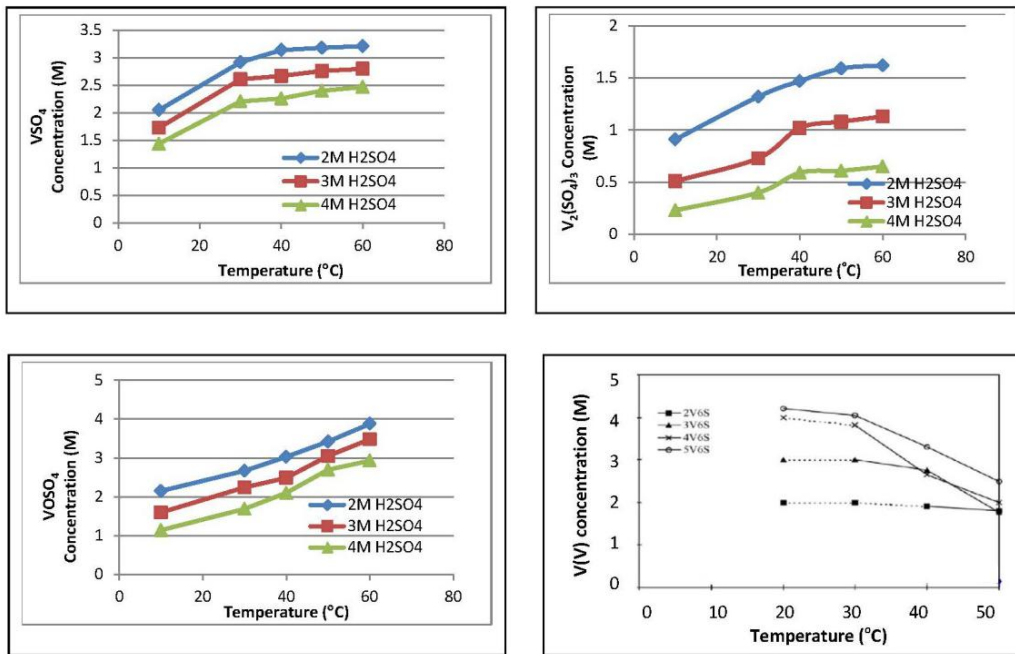
Figure 12. Vanadium ion solubility as a function of temperature and sulphuric acid concentration.
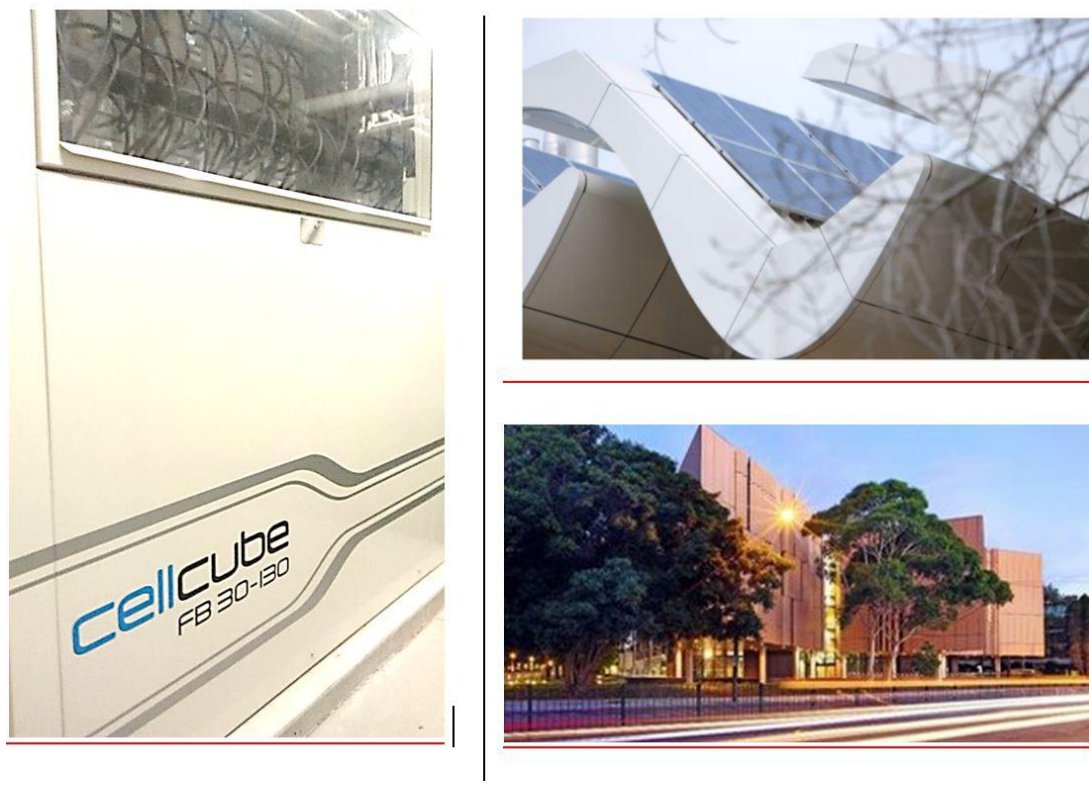
Figure 13. Three Building at UNSW Sydney with installed 130 kWh VFB and PV array on roof.

Tables

Table 1. Vanadium Production as a By-product (Habashi, 2002)

Raw Material	Coupled Product	Vanadium By-product
Titanomagnetites	Iron/steel	Vanadium slag
Mineral oils	Energy/petrochemicals	Fly ashes, boiler residues
Uranium-vanadium ores	Uranium	Petrochemical residue
Bauxite	Alumina	Vanadium salt
Phosphates	Phosphorus	Vanadium-containing Fe-P salamander
Lead vanadates	Lead, zinc	Vanadium slag

Table 2. Whole Rock Analyses of Vanadium-Rich Selected Samples from the Bell River and Doré Lake Complexes (Taner et al., 1998)

Sample	54	99	56	57
SiO_2	19.97	6.42	8.84	7.19
TiO_2	8.49	14.21	14.36	15.21
Al_2O_3	9.64	2.99	6.45	6.33
V_2O_3 *	0.49	0.59	0.52	0.66
Fe_2O_3**	50.37	69.38	60.71	64.17
MnO	0.24	0.32	0.28	0.32
MgO	2.94	3.53	2.45	2.25
CaO	4.13	1.28	1.72	1.38
K_2O	0.05	0.01	0.03	0.04
Na_2O	0.69	0.01	0.2	0.1
P_2O_5	0.02	0.01	0.01	0.01
S	0.94	-	0.18	0.19
LOI	1.53	1.23	0.45	0.74
Total%	99.5	99.97	96.2	98.59
Selected trace elements (ppm)				
Cr	18	126	203	213
Mn	1758	2870	2134	2210
As	15	<5	32	42
Sc	22	7	23	23
Co	127	111	115	143
Ni	60	193	69	83
Pb	19	<2	10	19
Cu	145	406	42	30
Zn	275	57	234	274

Au	2	38	<1	<1
Pt	<20	<5	<5	<5
Pd	<20	<1	<1	<1
* Equiv. V_2O_5%	0.59	0.71	0.63	0.8

Samples 54 and 99: Matagami; Samples 56 and 57: Chibougamau.

Analytical methods: whole-rock analyses were done by Intertek Testing Services-Chimitec at Val d'Or, Québec, Canada; major elements by XRF, selected trace elements by ICP-AES, S by Leco, V, Cu and Zn by atomic absorption (AA), and Au, Pt and Pd by pyroanalysis.

Table 3. Electron-Microprobe Analyses of Magnetite, Ilmenite and Mixture of Magnetite/ Ilmenite within Magnetite Containing Ilmenite Lamellae (Taner et al., 1998)

	Magnetite	Ilmenite	Mixture	Mixture
MnO	0.06	1.05	0.88	0.37
FeO	33.45	44.01	28.17	42.92
ZnO	0.20	0.00	0.19	1.02
Al_2O_3	0.97	0.01	0.68	2.21
Fe_2O_3	62.23	3.62	34.58	38.33
V_2O_3*	1.16	0.15	0.77	1.00
TiO_2	2.43	50.56	32.44	13.77
SiO_2	0.05	0.01	0.05	0.06
Total %	100.65	99.63	97.76	99.68
		Formula Contents		
Mn	0.00	0.02	0.02	0.01
Fe^{2+}	1.06	0.93	0.62	1.35
Zn	0.01	0.00	0.04	0.03
Al	0.04	0.00	0.02	0.10

Fe^{3+}	1.78	0.09	0.68	1.09
V^{3+}	0.04	0.00	0.02	0.03
Ti	0.07	0.96	0.64	0.39
Si	0.00	0.00	0.00	0.00
Sum	3.00	2.00	2.00	3.00
O	4.00	3.00	3.00	4.00
*Equiv.V_2O_5%	1.41	0.18	0.93	1.21

Magnetite (average of 20 samples): Formula contents per 3 cations and 4 anions.

Ilmenite (average of 21 samples): Formula contents per 2 cations and 3 anions.

Selected analyses of magnetite/ilmenite mixtures (magnetite with ilmenite lamellae).

Table 4. Summary of Principal Markets and end-uses for Vanadium

- Vanadium-bearing products

Iron and steel

    -High-strength steels

    -Full alloy steels

    -tool steels

    -Carbon steels

    -Stainless and heat resistant steels

    -Cast irons

Other metals and alloys

    -Titanium alloys

    -Superalloys and hard-facing alloys

    -Aerospace engines

    -Airframe materials

Non-metal end-uses for Vanadium

    -Catalysts

    -Ceramic, glasses and pigments

    -Electronics

    -Batteries (e.g., vanadium redox batteries)

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