Materials availability and supply chain considerations for vanadium in grid-scale redox flow batteries

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Abstract:

Redox flow batteries (RFBs) are a promising electrochemical storage solution for power sector decarbonization, particularly emerging long-duration needs. While the battery architecture can host many different redox chemistries, the vanadium RFB (VRFB) represents the current state-of-the-art due to its favorable combination of performance and longevity. However, the relatively high and volatile price of vanadium has hindered VRFB financing and deployment opportunities. Here we evaluate the vanadium supply chain to understand how it enables or constrains VRFB advancement and assess opportunities for accelerated growth. We find that – while vanadium may not be scarce – its abundance is confounded by highly concentrated production coupled with the disperse nature of sources suitable for potential supply increase. These factors challenge rapid growth, limiting deployment rate and magnitude. We estimate gigawatt-hour deployment scales are feasible over the next decade, which would represent marked expansion of the RFB industry and drive down system costs substantially, though this would require growth rates above historical averages. Accordingly, we review opportunities to accelerate supply chain growth and economic strategies to stabilize the market. Finally, we posit terawatt-hour deployment scales will be challenged by vanadium market conditions and, even, resource availability, motivating the continued efforts developing next-generation RFB chemistries.

Keywords: vanadium supply chain, vanadium redox flow battery, long-duration energy storage, compound annual growth rate

I. Introduction

Human activities such as agriculture, transportation, industry, residential and commercial operation, etc., all require energy, and global economic growth is only expanding the demand. While the power sector that procures, converts, and distributes energy to these critical markets was historically built on fossil-fuel burning technologies, the desire to prevent climate change is driving the decarbonization and, as a method of achieving this, electrification of the grid. To this end, considerable progress has been made in the development of renewable energy technologies; however, their significant penetration in the grid (> 60%) will be unsuccessful without complementary strategies to ameliorate their inherent intermittency that can misalign supply and demand. There are many approaches to overcome this mismatch, including upgraded transmission and distribution networks, demand-side energy management, overbuilding renewable capacity, and, the focus of this work, energy storage [1,2]. Since the grid hosts an array of services that vary in their operational characteristics and requirements, a diverse portfolio of storage solutions – varying in performance, frequency of use, cost, and scale – is needed [3,4].

Redox flow batteries (RFBs) are one promising storage solution, particularly attractive for emerging longer duration (i.e., > 5 hours) applications such as baseload renewable support (e.g., time-shifting supply and meeting peak power demand) [5]. RFBs use charge-storing chemical species dissolved in two liquid electrolytes, often referred to as "positive" and "negative" based on their relative electrode potentials. In the unique RFB architecture, electrolyte is stored in external tanks and circulated through a power-converting reactor, where the active species are oxidized and reduced to alternately convert electrical energy to (during charging) or from (during discharging) chemical energy. While flowing through the reactor, the two electrolytes are separated by a membrane while undergoing reduction and oxidation (or "redox") reactions on the surfaces of porous electrodes. Ions cross the membrane to balance charge between the two electrolytes, while the charge-storage species are ideally blocked through various exclusionary mechanisms (e.g., size, charge, etc.). The RFB architecture facilitates a number of unique benefits, including: the decoupling of the power and energy capacities, which provides flexibility and cost-efficiency in meeting a wide range of durations; the ability to host a significant range of chemistries and therefore explore a wide design space of cost and performance metrics; enhanced safety as compared to other conventional batteries (e.g., LIBs); and targeted component maintenance [6,7].

The latter of these benefits allows RFBs to remain cost-competitive in long-term operation despite experiencing relatively rapid capacity fade. A dominant fade mechanism is electrolyte degradation via crossover – undesired permeation of the active species through the membrane due to pressure, electrostatic, and diffusion driving forces [8] – which can often halve capacity in timescales as short as months [9]. Crossover is the result of using imperfectly selective membranes, which are often favored because they improve power performance and efficiencies [8]. With the RFB architecture, these losses can be remediated efficiently by performing direct maintenance to or, in the worst case, replacing a decayed electrolyte without altering other system components [7]. The ability to perform targeted maintenance is beneficial to RFBs as a technology platform and further promotes the development of chemistries whose long-term operation can be supported by simple, reliable, and inexpensive methods of electrolyte management, though few strategies have been developed so far. One of the few chemistries for which robust remediation techniques exist is the vanadium or all-vanadium RFB (VRFB).

The VRFB, originally pioneered in the 1980s by Skyllas-Kazacos, has been the state-of-the-art for decades and is the most commercialized RFB chemistry [10]. The VRFB uses the following two half-reactions for discharge (forward direction, left to right) and charge (backward direction, right to left) on the positive (Equation 1) and negative (Equation 2) sides of the electrochemical cell:

$$VO_2^+ + e^- + 2H^+ \leftrightarrow VO^{2+} + H_2O \qquad E^0 = 1.0\,V \quad \textbf{(1)}$$

$$V^{2+} \leftrightarrow V^{3+} + e^- \qquad E^0 = -0.26\,V \quad \textbf{(2)}$$

where E^0 refers to the standard reduction potential of the half reaction (versus the standard hydrogen electrode). The VRFB can achieve relatively high energy and power densities, as compared to other RFB chemistries, due to its cell voltage (~1.4 V at open circuit [11,12]), solubility (up to 2 moles of electrons per liter [13]), and current densities (state-of-the-art demonstrations maintain >90% energy efficiency at 200 mA/cm^2 [14]) under typical operating conditions (e.g., at room temperature, in strongly acidic electrolyte of ≥3 M H_2SO_4). In addition to these competitive metrics, the relatively extensive development of this chemistry is due to the resiliency of the VRFB as a "symmetric" chemistry, where all active species are based on a single parent compound [15]. The benefit of this chemical configuration is that losses due to active species crossover can be recovered via "rebalancing": the transfer and recharging of partial or full volumes of electrolyte between the two reservoirs to balance the concentrations and charges of active species [15,16]. Rebalancing allows for indefinite crossover remediation and, thus, lifetime utilization of the same, original electrolyte (assuming other forms electrolyte degradation are managed) [17]. To date, only a few redox chemistries have been demonstrated in a symmetric [13,18–24] or pseudo-symmetric (i.e., mixed electrolytes) [25–29] battery configuration, and vanadium remains the archetypical representation.

Despite the development of a strong candidate chemistry (i.e., the VRFB), RFB adoption has been limited due, in part, to the low demand for long-duration energy storage [30]. While the total scale of RFB installed capacity – from projects that have been deployed, contracted, announced, or are under construction – has recently reached the order of gigawatts at the time of writing, it still accounts for less than 2% of all energy storage systems globally (with most of these systems, including the RFBs, designed to operate at durations < 5 hours) [31]. While the majority of this capacity is pumped hydroelectric storage, due to its relative maturity, the electrochemical storage space is dominated by lithium-ion batteries (LIBs). Of the limited number of RFB systems that are already on-line, most have been operating for less than 10 years, contributing to a broad perception of technological immaturity and, thus, risk of investment, despite the attempts of VRFB companies to build the confidence of customers and investors with insurance and warranty policies [30,32]. While the vast majority of RFB installations are indeed VRFBs, due to its high technology-readiness level and low operational costs, the high upfront cost of the cell-level system, particularly at shorter durations, has hindered deployment opportunities. The current market price of vanadium translates to a total VRFB electrolyte cost of approximately 125 $/kWh [33,34], which is close to the price of some entire, state-of-the-art LIB packs (whose cost continues to decline, driven primarily by electric vehicle demand) [35]. In addition to high vanadium price, price volatility is cause for further concern. While historically the market price of vanadium, shown in Figure 1 as vanadium pentoxide (V_2O_5, a common vanadium product sold on the global market [34], though other vanadium products can be used to make VRFB electrolyte as discussed in the "Current landscape…" section), has demonstrated notable volatility, the last five years have been particularly unstable with a 10× difference between the minimum and maximum [34]. Though the current price of VRFB electrolyte (125 $/kWh) already challenges competitive grid storage, it represents a historic low for the last five years and may spike even higher in the future. This uncertainty alone can make investments in VRFBs less attractive. However, while new chemistries are being proposed that use lower-cost and higher-abundance materials, many of these efforts are at earlier stages of technology readiness, as compared to the VRFB, and while the issues they face may be known, solutions have yet to be fully developed preventing near-term deployment. For example, recent studies show the costs to manufacture electrochemical-grade, organic or organometallic active species can be substantial [36] and have more complex decomposition processes that are difficult to remediate [37,38]. Other research into chemistries that use stable, inorganic materials reveals issues such as competing parasitic reactions and, in the case of hybrid systems with deposition/dissolution reactions, difficulties preventing dendrite formation without severely limiting operating current densities [39,40].

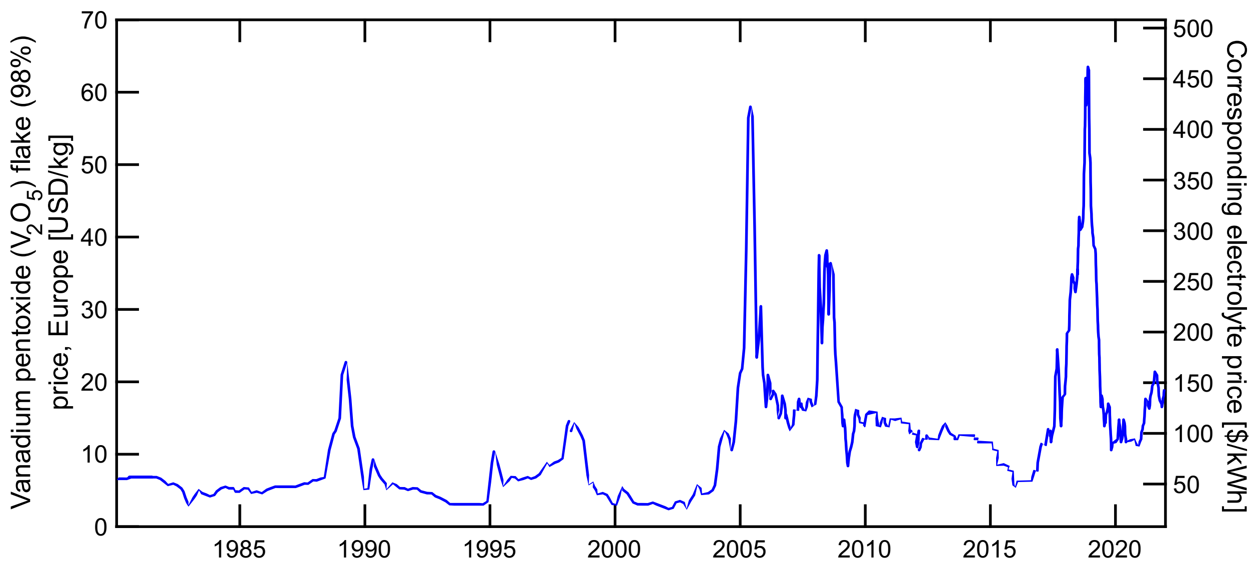

Figure 1 – Vanadium pentoxide (left y-axis) and corresponding VRFB electrolyte (right y-axis) prices in Europe from 1980 through 2021. Prices for ferrovanadium during this period follow nearly identical trends [34].

With growing demand for stationary energy storage, VRFBs may play an important role in near-term decarbonization efforts, making it important to consider the factors that impact their scalability. Currently, the price of vanadium (both in magnitude and stability) has invited concern regarding the deployment potential of VRFBs. To this end, we explore the vanadium supply chain to understand the nature of the historically high and volatile vanadium price. Supply chain studies have provided useful, research-driving insights for related technologies such as LIBs (e.g., concerns with the cobalt supply chain [41] have motivated research into alternative chemistries that minimize or avoid its use [42]). Such analyses have been lacking in the RFB field; while some recent studies have explored the vanadium supply chain, these have focused on the environmental, health, and safety considerations of vanadium production and VRFB operation [43–48]. Here, we focus on the production scale and growth rates needed to deploy sizable amounts of VRFB storage and examine opportunities to expand and stabilize the vanadium supply chain via the development of various supply streams and employment of economic hedging strategies. We believe these analyses can inform and drive the broader-scale deployment of RFBs.

II. Current landscape of the global vanadium supply chain

The United States Geological Survey (USGS) provides insight into the global production and resources levels for vanadium and other elements utilized in various battery technologies (Figure 2) [49,50]. Here, "global resources" are defined as concentrations of a geologic commodity in both discovered and undiscovered deposits (i.e., a "best guess") "in such form and amount that economic extraction … from the concentration is currently or potentially feasible" [49], though this value is generally an underestimation and typically grows with demand for a particular material (as demonstrated by the correlation between resources and production quantities across the minerals shown in Figure 2). Vanadium is considered relatively abundant and has many orders of magnitude greater global resources than scarce materials such as platinum group metals (PGMs, common catalysts in clean energy conversion and storage technologies). The world production and resources of vanadium are similar to those for critical LIB materials (i.e., lithium, cobalt, and, to a lesser extent, nickel), though these elements are one or more orders of magnitude less abundant than elements like sulfur, iron, zinc, copper, and manganese, which are the focus of many next-generation battery chemistries [40,51,52].

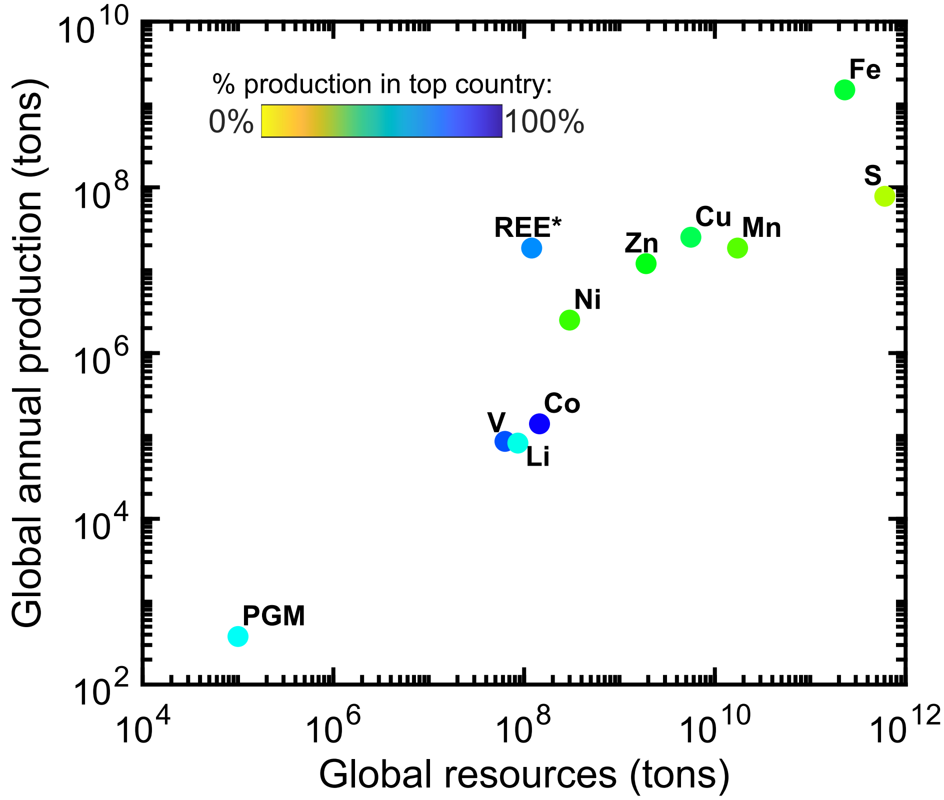

Figure 2 – 2020 global annual production (y-axis) versus global resources (x-axis) of vanadium, elements widely used in current Li-ion battery technologies, and minerals common to emerging energy storage technologies (in units of metric tons) [49,50]. The color of each element's market corresponds to the production concentration (*i.e.*, the percent of production coming from the top-producing country), as measured by the color bar. REE and PGM refers to rare earth elements and platinum group metals, respectively. Note: the global "reserves" (fraction of total resources that are currently economically recoverable) is used as the x-axis input for REEs, as total resources were not reported. Similarly, the "refinery production" (as opposed to the "mine production") was used for the y-axis input for Cu.

While vanadium may not be scarce, its abundance is confounded by highly concentrated production coupled with the dispersion of sources of potential supply increase, both of which can cause market instability and insecurity that translates into high and volatile prices. The color of each element in Figure 2 indicates the percent of total production coming from the top-producing country. Vanadium production is one of the most highly concentrated, with 62% of production originating from one country (exceeded only by cobalt at 68%), compared to the most abundant and produced minerals like sulfur, for example, for which the leading country is only responsible for 22% of global production. Vanadium production is concentrated in China (62%), Russia (21%), South Africa (10%), and Brazil (7%), where the parenthetical percentages represent each country's proportion of global vanadium production [53]. With so few countries dictating the production, the global vanadium market has experienced strong price volatility in response to local changes (see Figure 1) [47], and this uncertainty increases risk for investments in large-scale and capital-intensive VRFB systems to attract investment. Like many other energy-relevant minerals, this geographic concentration of production necessitates dependence on global supply chains. For this reason, vanadium was declared one of 35 "critical minerals" – minerals that are deemed vital to the Nation's security and economic prosperity but are primarily imported to the US – by the US Department of the Interior in 2018 [54].

An understanding of the current approaches to vanadium beneficiation helps to further illuminate the global supply chain. In general, vanadium must be extracted from vanadium-bearing compounds, of which there are two categories. The first is mined shale- and sandstone- hosted deposits, from which vanadium is currently recovered most often as vanadium titanomagnetite (VTM). The other category is vanadium-bearing waste products of carboniferous materials (e.g., coal, crude oil, oil shale, and tar sands), typically residues from burning and refining oil herein referred to as "secondary sources" [48,49]. The vanadium content of these materials can vary widely: generally, minerals from the earth contain ≤ 5 wt% V_2O_5, while slags and other waste streams are often more concentrated. Because of the low grade of vanadium found in minerals, mining of vanadium is often performed indirectly as a compliment to other materials (e.g., iron for steel). Thus, there are three pathways for vanadium production (Figure 3): 1) co-/by-product production in steel mills (75% of global production), 2) mines dedicated principally, by revenue, to vanadium production (10% of global production), and 3) secondary sources (15% of global production) [45]. All three methods use common extraction and refinement techniques. In general, roasting (oxidation at high temperatures) is followed by leaching, where the vanadium is dissolved into an acidic or basic aqueous phase. The vanadium is concentrated and recovered via solvent extraction or ion-exchange processes, after which it is precipitated as ammonium metavanadate (AMV, NH_4VO_3) or ammonium polyvanadate (APV, $[NH_4]_2V_6O_{16}$). From there, the APV or AMV precipitate is de-ammoniated and fused to produce vanadium oxides (typically V_2O_3 or V_2O_5) or ferrovanadium (via various thermal processes that ultimately react the vanadium oxide products with some iron-containing material, usually in the presence of lime), which are then sold to vanadium consumers [55]. For this work, we report vanadium content in terms of V_2O_5, as this is a common vanadium product sold on the global market and is typically used for such metrics, though trends and insights regarding the vanadium market broadly apply to all of these vanadium products [34]. A comprehensive review of vanadium production methods is beyond the scope of this work, but can be found in the literature [48].

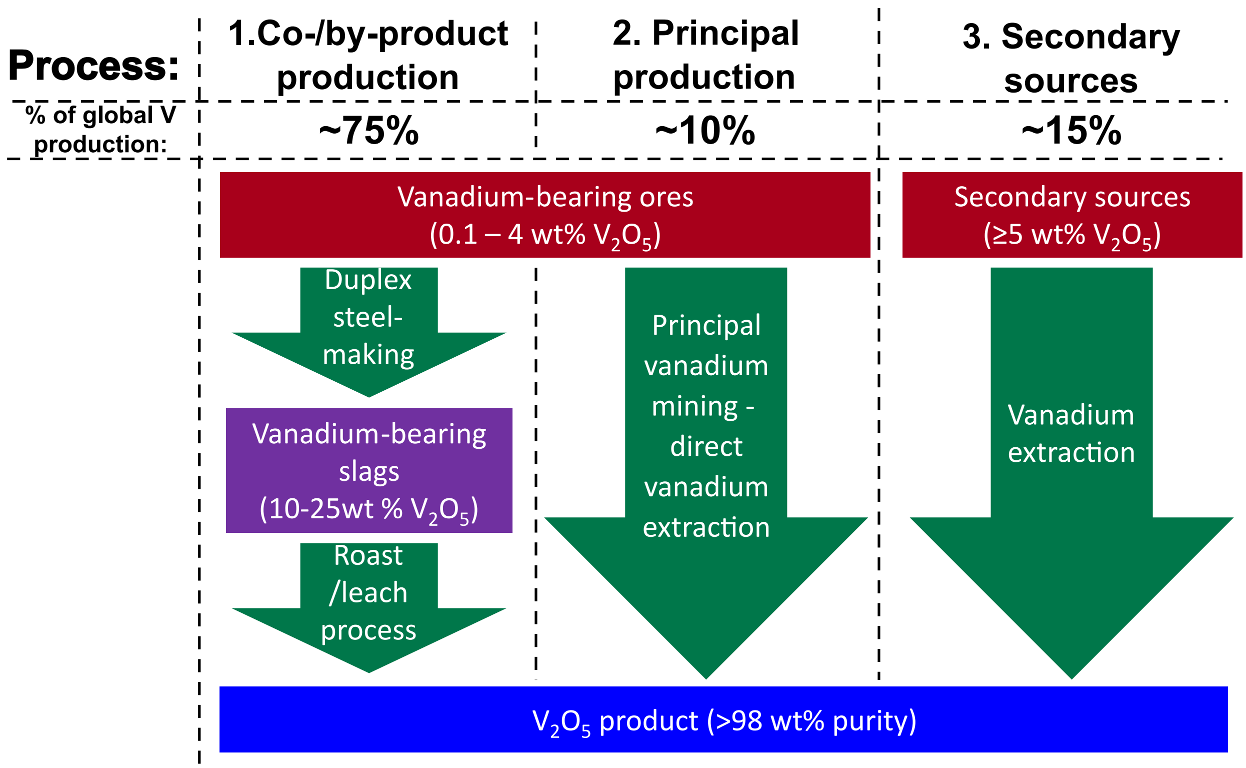

Figure 3 – Schematic of the three main production routes for vanadium pentoxide (V_2O_5).

Principal production (*i.e.*, mining ores for the principal purpose – based on the resulting revenue – of extracting, refining, and selling its vanadium content) contributes the lowest quantity to global production (ca. 10%) because the low grades or concentrations of vanadium in mined precursors make vanadium recovery uneconomical in most cases [46]. Currently, principally-mined vanadium mainly comes from Brazil, with the majority of operations run by Largo Incorporated, and South Africa, run by Bushveld Minerals and Glencore [56,57]. Secondary sources account for a similarly small portion (ca. 15%) of vanadium supply, broadly consisting of vanadium-rich slags and fly ash from burning petroleum products – a process which is often executed at power stations or at petrochemical factories – mainly heavy, "sour" crude oils found in the Caribbean (e.g., Venezuela and Mexico), Canada, as well as parts of the Middle East (e.g., Kuwait and Jordan) [45,58,59]. Co-/by-product production, defined as the extraction of a mineral in the process of mining and producing another mineral, represents the vast majority of the vanadium market (ca. 75%). The distinction between co- and by- products lies in the value of the additional material: co-products carry similar value to the principal material(s) they are produced with, while by-products generate less revenue than the principal material(s) [60]. In the case of vanadium, it is produced as a result of iron extraction for steel-making: iron is extracted from magnetite ores for further use in steel, though those ores may also contain vanadium that can be recovered. The crux of this process is oxidation, primarily to remove the carbon from the ores. However, the execution of this oxidation is crucial to facilitating or prohibiting economic vanadium recovery: the mills that produce the ~75% of global vanadium supply utilize a "duplex process," where an additional oxidation step is imposed first to selectively oxidize vanadium, enriching it into the slag phase as oxides where is it more easily recovered [48]. This process is a sensible and profitable choice for ore precursors with notable vanadium content, as it allows for economic recovery of the vanadium. Other facilities use a single-step method that is currently prohibitive for viable vanadium recovery as it adds calcium (to suppress the slag's ability to solidify upon encountering the relatively cooler oxygen [61]), which creates vanadium-calcium bronze complexes that are difficult to break apart [62,63]. Indeed, conversations with industry experts revealed that slags containing vanadium-calcium compounds are sitting idly at steel-making factories because the vanadium cannot be economically extracted. This implies that were VRFB deployment to increase, this supply could be brought online in response to that demand, if the economics of vanadium extraction from this source can be made viable.

Supply chain complications can arise when the majority of a material's production is as a co-/by-product [41], as the price or demand for a co-/by-product does not strongly affect its supply (at least in the short term). Vanadium is further complicated by entanglement between supply (which, as discussed, is mainly as a co-/by-product from steel-making) and demand, as currently ~90% of vanadium production goes to steel manufacturing (i.e., alloying to increase steel strength) [64]. Further inspection of the vanadium co-/by-product supply distribution reveals more causes for concern: while co-/by-product production represents the majority (75%) of the global vanadium supply, conversations with industry experts revealed that this stream is concentrated around ~10 steel mills, primarily in China and Russia. Such severe concentration reflects extreme precarity in the supply chain and can intensify volatility in supply and price. For example, the price spike that began in 2016 (Figure 1) was partially a result of the bankruptcy-induced closure of Highveld Steel & Vanadium in South Africa in 2015 [65], previously the world's largest producer of vanadium slag from steel production [66], which caused an ~11% decrease in global vanadium production [67]. This decrease in supply was compounded by other mine closures in China due to increased enforcement of environmental regulations [67,68]. Supply has remained depressed for years [67] and has only begun to rebound as of 2019 [49], likely due to increasing principal production in Brazil led by Largo Incorporated. Simultaneous to these supply constrictions were increases to demand in late 2018 due to revised Chinese "rebar" standards (regarding steel strength) that promote greater use of vanadium in high-strength steel alloys [67,69]. The combination of circumstances ultimately led to the price spike in the final months of 2018, which peaked at 10× the price relative to early 2016 [34] (Figure 1).

III. Quantitative analysis of vanadium supply chain scale-up needed for VRFB deployment targets

The expansion of VRFB production and deployment depends on the ability to increase the scale of vanadium production. To illustrate the required expansion of vanadium production required by a targeted level of deployment we assume, following Kavlak et al. [70], that the production of vanadium increases at a uniform compound annual growth rate (CAGR) year over year. In terms of the CAGR, the production in year n, p_n, is related to the present-day global production, p_0 by,

$$p_n = p_0\,(1 + CAGR)^n \qquad \textbf{(3)}$$

where $p_0 = 8.6 \times 10^7$ kg(V) per annum (in 2020 [49]). Assuming only new vanadium supply is available for VRFBs, one must specify the fraction of new vanadium production going towards VRFBs (f), as well as the materials intensity (I), which is a conversion between the amount of vanadium needed for a given amount of storage deployed:

$$I = \frac{2(MW)}{n_e F U \chi} \quad \textbf{(4)}$$

The calculation of I depends on the molecular weight of vanadium ((MW), 0.051 kg mol^{-1}), the open-circuit cell potential (U, 1.4 V), the depth of discharge (χ, 0.8), the number of moles of electrons transferred per mole of vanadium (n_e, 1 mol(e$^-$)/mol(V)), the Faraday constant (F, 96,485 C/mol(e$^-$)), as well as other necessary unit conversions [12]. Further, the factor of two in the numerator accounts for the two electrolyte tanks per system (as vanadium is used on both sides of the cell). The value of I is found to equal 3.4×10^9 kg(V) per TWh of energy storage capacity. Next, the VRFB capacity that could be deployed in a future year n (d_n, in units of energy/year) is calculated by scaling p_n by f and I^{-1}:

$$d_n = \frac{p_0 f}{I} \left((1 + CAGR)^n - 1\right) \quad \textbf{(5)}$$

The subtraction of one is included to eliminate the present-day production quantity of vanadium from consideration for use toward VRFB deployment, as we assume existing supply is already accounted for. To determine the cumulative deployment in year N (D_N), the annual deployments (d_n) from each year beginning now through year N must be summed:

$$D_N = \sum_{n=0}^{N} d_n \quad \textbf{(6)}$$

Using the identities $\sum_{n=0}^{N} x^n = \frac{x^{N+1}-1}{x-1}$ and $\sum_{n=0}^{N} 1 = N + 1$, we find a closed-form, analytical solution for D_N:

$$D_N = \frac{p_0 f}{I} \left(\frac{(1+CAGR)^{N+1}-1}{CAGR} - 1 - N\right) \quad \textbf{(7)}$$

Equation 7 is used to determine the CAGRs needed to achieve varying total deployment scales in 2030 (Figure 3a, N = 10 years) and 2050 (Figure 3b, N = 20 years), relative to 2020, under varying scenarios of fractional new vanadium supply going toward VRFB deployment. Where applicable, the resource limit (i.e., the case where all the global vanadium that can be currently or potentially economically extracted is mined) under each fractional scenario is shown as a vertical dashed line.

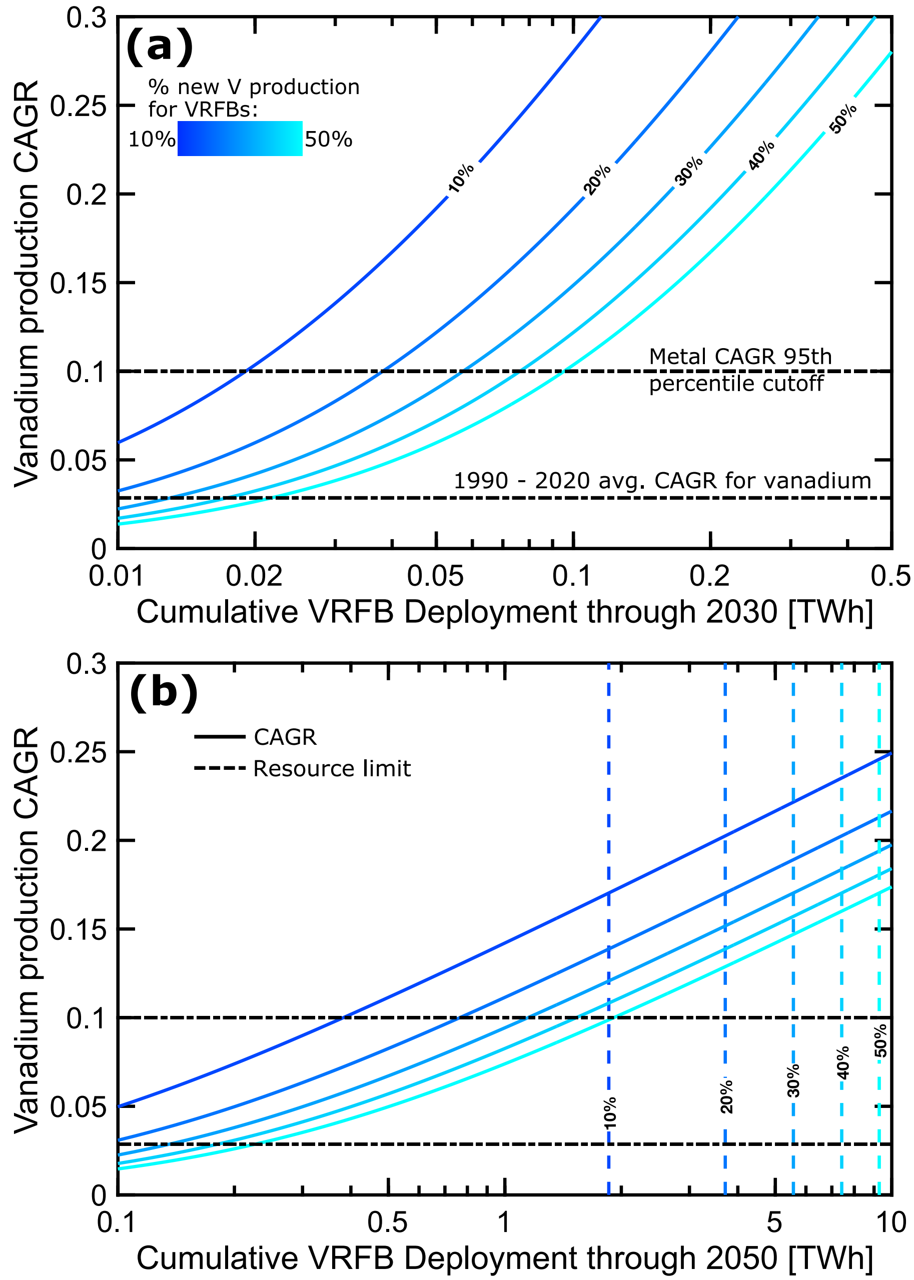

Figure 3 – Compound annual growth rate (CAGR) of vanadium production needed to achieve various amounts of cumulative VRFB deployment by 2030 (a) and 2050 (b), relative to 2020, based on various scenarios of new fractional production routed to VRFB production over other applications (various shades of blue). The 2050 plot also shows the resource limit under each scenario (vertical dashed lines). The black horizontal lines show relevant historical CAGRs.

Historical ranges for the growth rates of vanadium and other metals provides insight into the growth potential of vanadium production. The blue contours represent the fraction of new production going towards VRFBs, the relevant magnitude of which depends on the competition between vanadium for steel and vanadium for VRFBs, although other use-cases may appear in the future. At present, about 90% of vanadium production goes to steel manufacturing and this demand is likely to grow in the future given continued global economic development as well as a shift towards higher-strength steel in construction to reduce total material requirements [71]. While there are opportunities to substitute vanadium with other alloying elements (*e.g.*, manganese, molybdenum, niobium/columbium, titanium, and tungsten) – indeed, some steel mills in China have switched from ferrovanadium to ferroniobium due to high vanadium prices [49] – it does not seem that such substitutions will allow significant vanadium supply to be re-routed away from steel demand in the near future. Thus, a conservative (business-as-usual) estimate would assume that steel will continue to drive the demand for vanadium at historic rates and only about 10% of new vanadium production will be available for VRFBs. However, with growing energy and sustainability concerns, larger percentages of vanadium production (say, as much as 50%) may be diverted to VRFBs (likely influenced by national policy incentives), particularly if it is possible to more rapidly scale supply (as will be discussed in the next section). We can set a context for the various CAGR scenarios displayed in Figure 3 via the results of a study on metal production requirements by Kavlak *et al.*, which determined that only the top 5th percentile of the 32 metals analyzed by the study sustained average CAGRs greater than 10% over 18 year periods (analyzed from 1972-2012), with none exceeding 15% [70]. Comparing vanadium production from 2020 to that of 1990, we compute an average CAGR across this 30-year period of 3.55% [49,72]. The year-to-year growth rate is generally highly variable, and vanadium is no exception: some years have seen greater than 30% or 40% growth, though the compound annual growth rate over longer time horizons averages much lower. This is an important distinction captured by the CAGR, as sustained growth of the supply chain is critical to supporting VRFB growth. Notably, the last two years of reported data (2019 and 2020) have shown sizable growth, ca. 20% per year, mainly due to rapid expansion of Chinese co-/by-product production to support record domestic steel manufacturing volumes as a response to stimulus measures triggered by the COVID-19 pandemic [73]. While promising, it is unclear if this growth rate can be maintained. In light of this analysis, we can now evaluate our ability to scale up production and deploy various amounts of VRFB storage.

Looking, for example, at 10% CAGRs as an optimistic value, new VRFB deployment is limited (i.e., $f \leq 50\%$) to ≤ 100 GWh by 2030 and ≤ 2 TWh by 2050. At the time of writing, there are currently ~100 MWh of RFBs in operation globally [31], and projections for global grid storage demand are anticipated to be at hundreds/thousands GWh- and tens/hundreds TWh- scales by 2030 and 2050, respectively [60]. The bounds to production scalability may not limit VRFB deployment ambitions in the near-term (i.e., 2030), particularly as relevant applications (e.g., renewables support) for long duration energy storage are still nascent. Deployment at the 10's-100's of GWh level would represent promising scale-up for the RFB industry and could drive down manufacturing costs and, potentially, increase vanadium demand in market-driven ways (i.e., reducing price volatility and driving increase in supply). There is also a broader benefit to VRFB development that is a testament to the versatility of the RFB platform: RFBs represent an architecture that can house a diverse array of chemistries, and the cost reductions and technical advancements from accelerated VRFB deployment could be translated to earlier stage RFB chemistries. For example, GWh-scale deployment of the VRFB could advance general efforts in cell and stack design and optimization, as well as reactor and electrolyte maintenance. Unfortunately, the longer-term (i.e., 2050) bounds – both those determined by realistic CAGRs and those imposed by the resource limits, which do not drastically differ in scale – are more limiting since they differ from the global demand projections for grid storage by about an order of magnitude. However, scaling VRFB deployment in the near-term will help drive down costs and reduce the perceived investment risks of RFB systems such that other lower-cost and higher-abundance chemistries may be used in these more distant horizons. VRFB systems could even be modified with a new chemistry, simply by replacing the electrolyte, 10+ years into the RFB's deployment, especially if the vanadium electrolyte is leased [74]. Thus, the VRFB is a well-developed system that could be used as an entry point for larger scale RFB deployment of other chemistries. Conversely, by 2050 it may become evident that systems previously projected to be promising and "low-cost" may in fact require prohibitively expensive active materials (e.g., costs to upgrade precursors are high or degradation requires too-frequent replacement of materials) or be unable to achieve necessary technical performance metrics. Many other RFB systems may ultimately struggle to compete with the high-performing VRFB system that already overcomes many challenges presented by other chemistries. In this sense these "limits" could spark meaningful growth to the VRFB and, potentially, RFB markets broadly that will catalyze important reductions in cost and perceived risk, facilitating further deployment.

IV. Opportunities to expand and stabilize the global vanadium supply chain

In this section, we look at opportunities to scale vanadium production more rapidly through expansion and de-concentration of the supply chain, as well as other market solutions to reduce the burden of the high and uncertain upfront cost of vanadium. We consider first expansion of by-/co-product production, then secondary production, and finally primary production of vanadium, after which we turn to other strategies to ameliorate vanadium price volatility and reduce up-front capital investment associated with VRFB deployment.

a. Vanadium production scale-up opportunities

To meet or exceed the limits identified for 2030 and 2050 deployment (which assume 10% CAGRs), production scale-up must accelerate relative to historic vanadium CAGRs (< 4%) [49,72]. Rapid supply chain growth relies on the expansion of existing vanadium production routes as well as economical beneficiation of new vanadium precursor sources. While vanadium is not scarce and exists in many regions of the world, it presents in low grades and thus is costly to extract. Prior to considering different routes for production expansion, it is useful to contemplate other metals that have historically shown high CAGRs and the factors that contributed to those growth rates.

Cobalt and indium are two metals produced as co-/by-products that have seen significant growth in recent decades due to drastic demand increases driven by technology adoption. The global production of cobalt, a critical component of positive electrode chemistries in advanced LIBs (e.g., lithium cobalt oxide, nickel-cobalt-aluminum, nickel-manganese-cobalt), has grown by over 7.5× (i.e., an average CAGR of ~8%) since the mid-1990's due to ever-expanding demand for LIBs in portable electronics, electric vehicles, and stationary energy storage [75]. Despite the increased demand, cobalt still is mostly produced as a co- and by-product of copper and nickel, respectively [41]. Similarly, indium production has experienced a CAGR of ~10% since the 1970's due to its use in semiconductors that underpin photovoltaic devices and electronic displays [70]. Indium is also produced predominantly as a co-/by-product of zinc. While co-/by-product production generally decouples its supply and demand, supply can still be driven by demand for some limited period of time: for example, Frenzel et al. showed how indium production has grown ~10× faster than production of its host material, zinc [76]. Such a phenomenon often results from increased demand for the material of interest (in this case, indium) that facilitates higher utilization and recovery rates of it from the host material (i.e., a higher percentage of the total amount of extractable co-/by-product is actually recovered from the host material than before, bolstering its production rate). Gao et al. reports that vanadium recovery from duplex steel slag is generally only ~50% (~80% recovery in each of three steps: reductive smelting, selective oxidation, and vanadium extraction), suggesting that it may be possible to increase vanadium recovery in existing production methods through process optimization [48]. However, there are other notable complications hindering the expansion and stability of these operations.

Expansion of co-/by-product production via duplex steel-making processes presents challenges based on its unfavorable economics. The duplex process is not the most efficient steel-making method, as it requires a multi-step oxidation of the steel to recover vanadium, thus necessitating additional capital and operating expenses while introducing more inefficiencies as compared to single-step processes [77]. Additionally, the iron content of vanadium-bearing titaniferous magnetite (VTM) ores – used for duplex steel-making as they enable vanadium recovery – is low, making VTM-based steel more expensive to produce [48]. While duplex mills may benefit financially from vanadium co-/by-product production, the primary driving force that will keep them operating is revenue from steel. Thus, duplex mills may have an inherent competitive disadvantage and single-step processes may ultimately displace these legacy technologies. These considerations have contributed to the low number of duplex facilities at present, could cause the closure of existing facilities (e.g., Highveld Steel and Vanadium, discussed earlier), and may deter the formation of new duplex operations in the future. Contrary to these points, sustained growth of global vanadium production by ~20% in both 2019 and 2020 was primarily due to expansion of co-/by-product vanadium from steel-making in China [73]. However, diversification of the supply chain is as important as sheer growth, so we turn our attention to other potential supply streams for the remainder of this discussion.

There are promising opportunities to expand and diversify supply via alternate methods for recovering vanadium as co-/by-products of other materials. First, other potential routes for vanadium production could lie in non-duplex steel-making processes. As discussed previously, many steel mines produce vanadium-calcium residuals that are currently unused due to the economic infeasibility of recovering their vanadium, though there are efforts to develop and scale-up vanadium extraction from such precursors: Neometals, an Australian company, claims to have developed a hydrometallurgical process to recover vanadium from these mono-process slags. The company recently partnered with Scandinavian mineral development company Critical Metals Ltd, which has executed a 10-year supply agreement with Swedish steel giant SSAB to access approximately 2 Mt of stockpiled high-grade vanadium-bearing slag from three operating steel mills [78]. While details on the Neometals process are not public, significant project challenges are anticipated including potentially prohibitive capital cost requirements (presuming the need for on-site smelters), as well as technical challenges in the vanadium recovery itself. Gao *et al.* also note that the low concentration of vanadium in most VTM-containing ore may limit principal production opportunities for the foreseeable future, and expanding the co-/by-production of vanadium with other valuable metals beyond iron for steel (*e.g.*, chromium, titanium, or manganese) may be necessary for rapid growth [48]. While co-/by-product production presents inherent challenges, diversification and expansion of the operations contributing to this stream would at least reduce the most imminent supply concentration problems.

Perhaps the most promising avenue for near-term growth and diversification of the supply chain is through secondary-source vanadium from oil. These precursors are attractive due to their higher vanadium content ($\geq$ 5% V_2O_5) that makes vanadium extraction more economical [58,59]. Conversations with industry experts revealed that while the precursor materials are generally wastes from burning and refining oil, they are currently sold to vanadium producers at market-based prices and used in smaller batches, making the cost to produce vanadium from these materials relatively high compared to other methods. Vertical integration of the vanadium recovery and production operations into existing oil refineries could significantly cut costs, as would expanding these facilities to process larger volumes of secondary-source precursors. While the anticipated modifications to the power generation infrastructure (i.e., decarbonization and electrification) may impact the operation of the fossil fuel industry and potentially disrupt the supply of secondary-source precursors, this stream could provide a bridge in supply while new technologies and methodologies for vanadium extraction from lower-grade precursors are developed (as discussed next). Without relying on techno-economic advances in vanadium recovery, this supply stream could rapidly expand and diffuse the distribution of vanadium production. Many countries that currently lack a domestic supply chain for vanadium would be suited to develop secondary-source vanadium production – for example, the US is a prime candidate due to its arsenal of oil refining facilities that are concentrated in the south of the country [46] – which could further advance the energy independence efforts of those countries if utilized for the deployment of VRFBs.

In the longer term, the largest potential to grow and stabilize vanadium production – contingent upon crucial technological advances in vanadium extraction and recovery from low-grade sources – likely lies in principal mining, as vanadium is relatively abundant globally with major deposits in each inhabited continent [80]. While vanadium mines have been proposed for decades, many have yet to be realized due to financing issues. Generally, mines are capital-intensive and require years of operation to pay back; for example, a 2011 report from the German Institute for Applied Ecology cites investment costs of $30,000 per ton of recovered capacity for rare earth element mines [81]. The ease or difficulty of financing the construction of a new mine is determined by a number of factors, but a critical piece is the feasibility study, which lays out the development and production schedules that are used to derive a cash flow model in order to determine the internal rate of return and payback period. The apparent inevitability of delays in announced principal vanadium mining projects across numerous locations is likely due to difficulty justifying the project economics found in these feasibility studies to investors, pointing to inherent challenges to extracting the relatively low grade of vanadium from precursor materials. However, if economic ways to recover vanadium from these mines could be found, it could create a sizable new supply stream.

Opportunities for new principal vanadium mining ventures exist in a range of locations – most notably in Australia, the US, and China – which could facilitate substantial supply capacity. Australia has substantial vanadium reserves, though no reported production in recent years, likely due to the lower vanadium concentrations present in their precursor supply: ~ 1% V_2O_5 content [82,83], as compared to ~ 2-3% in South Africa and Brazil (where the overwhelming majority of principal production currently occurs) [48]. Plans have been announced to develop three sizable vanadium mines: the "Australian Vanadium Project" in western Australia, the "Mount Peake Project" in northern Australia, and a mine at Saint Elmo in Queensland [82–84]. These projects are based on new proposed methods for vanadium extraction and recovery, though the technical details have not been publicly disclosed. While the projects are still in the planning stages, if completed, they are expected to collectively produce ~ 27,000 metric tons of V_2O_5 per year, which would represent an ~18% increase to the current global production of vanadium. While this represents a marked growth of the supply chain, continuous growth for at least 10-30 years would require new mines of this scale to come online annually, which appears to be challenging. Further, these mines have finite operational lifetimes of 10-50 years (i.e., until resources are depleted). However, circulation of their vanadium extraction methods could facilitate the market entry of other mines to sustain growth; in particular, principal production in the US and China. The US recently announced plans for a principal vanadium mine called the Gibellini project, to be located in Nevada's Battle Mountain region. The V_2O_5 content is low (< 0.4%), and anticipated production is ~ 4,600 metric tons of V_2O_5 per year [85]. Major reserves lie in China in the form of stone coal, which is an abundant resource (~62 billion tons) that contains ~ 1.5% or less V_2O_5 content, but currently only contributes ~10% of Chinese vanadium production [48].

This new supply will take time, as mines typically require 5-10 years to come online due to the lengthy approvals process through relevant regulatory avenues, which vary based on location and can take up to 50 years in the worst cases [81]. Thus, expansion of principal production should be expected to be a longer-term endeavor, which presents new challenges and risks to financing such operations in the first place as the vanadium demand may drop (*e.g.*, if the VRFB is supplanted by another RFB chemistry or a different energy storage solution). Further, this timeline is already optimistic, as it does not account for the time needed to advance vanadium recovery technologies that make these mining approaches economically viable. Economic recovery of low-grade vanadium depends on the same methodologies used in current predominant schemes of vanadium extraction, though the lower grade makes the process less profitable. In particular, transportation of precursor material can become prohibitively expensive if the grade is too low, as costs scale in $ per unit weight (hence why co-/by-product production is attractive, as it reduces the deadweight fraction). Thus, the burden of the added deadweight must be offset by higher efficiencies, recovery rates, and lower costs in processing the materials. High transportation costs may necessitate the development of processing sites that are mobile and/or co-located with the mine. This is a route many new mines are taking, though it adds significant capital requirements on top of already expensive projects.

We note that, beyond the economics of vanadium recovery, there are also a multitude of environmental, health, and safety concerns to be considered in vanadium production processes (*e.g.*, production of pollutant gases in duplex recovery, ecological and geological impacts of building and operating mines, etc.). While such matters are beyond the scope of this work, future research may consider quantifying the associated risks and costs in order to more holistically determine the best paths for vanadium supply chain expansion. Further research and development efforts to mitigate these effects in existing processes are similarly critical, not only to address the direct impact of these factors but also because they, if left unmitigated, have the potential to cause the closure of existing operations as regulations become stricter (as seen recently in China [68]). We recommend works by White et al. and Gao et al. for more information on this topic [45,48].

b. *Economic strategies to mitigate price volatility and reduce the upfront cost burden of vanadium*

While supply scale-up is necessary to augment VRFB deployment and will likely help stabilize the market, there are other potential more-immediate solutions to mitigate volatility of vanadium prices. One tactic is vertical integration, where a corporation owns the vanadium mining and refining company as well as a VRFB or vanadium electrolyte company. While logistics may vary, vertical integration is expected to enable the battery vendor to reduce the impact of vanadium price volatility and plan long-term technology pricing trajectories. While vertical integration may also facilitate lower vanadium prices to the VRFB company, this is not guaranteed and depends on the outlook of the overarching corporation regarding profit allocation. Another layer of vertical integration could easily be incorporated to process and recycle the spent vanadium electrolyte at the end of life – whether purifying for re-use or recovering and reselling the vanadium for other applications – which requires unique expertise that could be shared by a vanadium miner and refiner [86]. This approach is being pursued by two major principal vanadium producers, Largo

Incorporated and Bushveld Minerals, who have created subsidiaries Largo Clean Energy (which will sell VRFB systems, a result of Largo's acquisition of VRFB company Vionx in late 2020 [87]) and Bushveld Energy (which will sell VRFB electrolyte [88]), respectively. A related method to prepare vanadium supply for future demand and therefore reduce price volatility and uncertainty to the buyer involves hedging strategies such as futures contracts, which are agreements between suppliers and buyers to transact vanadium at a pre-determined price at some specified future time. Futures contracts are common in some commodity markets such as oil, precious metals (e.g., gold, silver, and platinum), agricultural products (e.g., corn), etc., and could potentially be employed in the vanadium industry. In fact, cobalt – a metal with a similar supply chain structure to that of vanadium, in many ways, as discussed previously – can now be bought and sold via a futures contract launched in late 2020 [89]. Even prior to this development (i.e., as of 2010), cobalt became one of only two "minor metals" (along with molybdenum) traded on the London Metal Exchange, the largest global market for a range of metals. The transparency of such a market can help stabilize the supply chain, and indeed the cobalt price volatility is more than a factor of three lower since 2010 than between 1970 and 2010 [41]. While more comprehensive economic analysis regarding the promise of these strategies for VRFB deployment is beyond the scope of this work, it should be explored by others with cross-disciplinary expertise.

In addition to its volatility, the magnitude of vanadium prices is an issue. While efforts to expand and stabilize the supply chain may help reduce vanadium prices in the long-term, any near-term expansion of supply may only occur as a response to price increases (e.g., to offset the more expensive recovery of low-grade principal production). Thus, the prohibitive price of vanadium may remain a separate issue from the supply chain challenges discussed here. One method to reduce the burden of the vanadium price does exist via a new market of electrolyte leasing, where a third-party company leases the vanadium – usually in the form of VRFB electrolyte – to a battery vendor or end-user. This reduces the upfront capital cost of the battery while increasing long-term costs (i.e., a shift of capital expenses to operational expenses) by introducing some recurring fee [90,91], which is attractive as it lowers the cost and risk of the required upfront investment for VRFB customers. In some schemes, a portion of the financial burden of leasing is shifted from the lessor to third-party investors who can buy and trade vanadium – akin to markets for other physical holdings, like gold – though it is held and maintained by the lessor, who simultaneously rents it out as electrolyte to VRFB customers [92]. These markets are new, and little has been published regarding their logistics or early-stage utilization and efficacy, though a few academic studies have demonstrated the techno-economic potential for leasing [33,93].

V. Conclusion

RFBs are a promising solution for grid-scale storage, with the VRFB being the most studied and deployed RFB chemistry due to its remarkable performance attributes and unique chemistry design. Despite these benefits, the high and volatile price of vanadium has remained a major impediment to VRFB (and, more largely, RFB) deployment. In light of this, we explored the causes behind the high and volatile price of vanadium and evaluated the outlook for growth and stabilization of the supply chain.

While vanadium is relatively abundant and found in many parts of the world, the difficulty lies in its economic extraction that currently prevents many low-grade vanadium precursors from being utilized. This issue has limited present-day supply mainly to co-/by-product production from duplex steel slag, where vanadium is extracted as a lesser-valued product along with iron for steel-making. Reliance on co-/by-product production presents inherent challenges due to a decoupling of supply and demand for vanadium, as supply is driven by demand for steel rather than demand for vanadium. What is of more immediate concern, however, is the concentration of this supply stream, as it comprises only ~10 mills (mainly in China and Russia), which together provide 75% of global production. Such concentration can create extreme volatility in supply that can in turn lead to surges in price, such as the 10x price spike of 2018. Further, it creates geopolitical vulnerability to importing countries and thus hinders efforts toward energy independence. Other minor contributors to vanadium supply come from principal production (mining of ores directly for vanadium) and secondary production from residues and wastes generated by the refining of vanadium-containing petroleum products.

We also sought to quantify market growth needed to achieve various cumulative VRFB deployment goals by 2030 and 2050. Metal supply chains rarely see CAGRs > 10%, and vanadium has demonstrated much more modest growth in the last 30 years (< 4%). As existing vanadium demand is accounted for (primarily by markets for high-strength steel), relatively rapid growth in supply is needed to achieve sizable future VRFB deployment. In the near-term (i.e., 2030), we find vanadium production scale-up is likely feasible to meet expected demand (up to 100 GWh). Deployment to this extent would certainly represent significant growth to the RFB market broadly and would have a notable effect in reducing both the cost of chemistry-unspecific RFB components as well as the perceived risk around RFB deployment, thus accelerating further RFB commercialization efforts. However, the long-term prospects are more restrictive: the relatively modest magnitudes of both existing vanadium production and historic rates of supply chain growth for metals limit feasible future VRFB deployment to only ~2 TWh by 2050. This diagnosis itself, as well as hopes of 10's-TWh or greater deployment scales, depend on growing the vanadium production scale more rapidly than it has historically (i.e., at a CAGR of ~10%), which largely relies on improving our vanadium recovery capabilities to utilize lower-grade sources of vanadium, making such efforts worthwhile recipients of more devoted research and development resources. Due to the low grades of vanadium found in natural precursors, economic vanadium production may always be dependent on co-/by-product recovery. While duplex steel co-/by-product production demonstrates poor steel-making economics that may make this supply precarious and less likely to expand, new avenues for co-/by-product production from alternate steel-making methods or with other metals can grow and diversify the vanadium supply chain. However, economical principal vanadium production is potentially within reach, with projects being announced across the world that would expand production capacity significantly. Further, production from secondary sources can help bridge supply, since development of these sources does not require major technological advancements. These principal and secondary vanadium sources have the potential to bolster US production capacities in particular; indeed, one US VRFB manufacturer has announced plans to domestically source all of their vanadium, implying the US vanadium supply chain is already growing [94]. Other economic strategies can help reduce price volatility and upfront costs of vanadium in the near-term, including vertical integration of VRFB companies, hedging supply/demand risk via futures markets for vanadium, and electrolyte leasing.

Ultimately, near-term decarbonization goals necessitate deployment of massive amounts of energy storage as soon as possible. The VRFB has the highest technology-readiness level of all RFB chemistries and its rapid deployment at reasonable and, per this study, feasible scales (i.e., up to 100 GWh by 2030) can help meet decarbonization goals while simultaneously promoting future, broader-scale RFB deployment by de-risking the technology and lowering costs for chemistry unspecific components. In tandem, the RFB community must also develop alternative chemistries (and operation and maintenance strategies to facilitate their viable long-term performance) based on lower-cost and more widely-available materials [38,95,96]. Ultimately, these RFB systems may prove to be more expensive or challenging to make and operate than previously thought [36], supporting the need for more expansive and rapid growth and stabilization to the vanadium supply chain.

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