Environmental Chemistry of Vanadium
Considerations for Risk Assessment

September 18, 2019

3:00pm Eastern

VPRA
Vanadium Producers & Reclaimers Association
www.vanadiumproducers.org

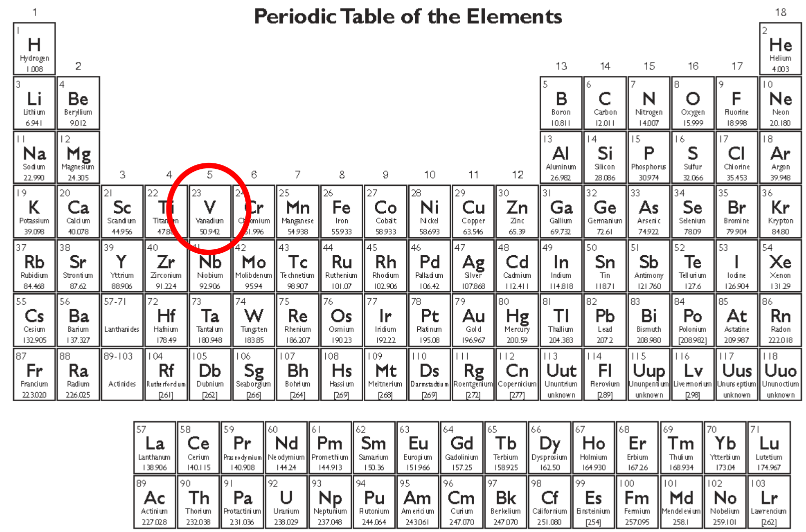
Agenda

- Introduction to VPRA
- Introduction to Vanadium
- Production and uses of Vanadium
- Vanadium in the Environment
- Vanadium Chemistry
- Vanadium Environmental Water Chemistry
- Vanadium Environmental Solid State Chemistry
- Implications for Risk Assessment
- Summary

Introduction to VPRA

- Vanadium Producers & Reclaimers Association
- North American Trade Association
- Small industry: 3 full members representing producers of Ferrovanadium, Vanadium Oxides and Vanadium Chemicals
- 231 total workers employed in the US
- No domestically-mined vanadium in the US
- Secondary recycling from petroleum waste streams
- ”Spent catalyst” would otherwise be a EPA Listed Hazardous Waste

Introduction to Vanadium



- Vanadium occurs naturally in approximately 80 minerals including sulphides, sulphates, silicates, oxides, phosphates and vanadates
- It is the 22nd most abundant element in the earths crust
- In the USA occurs commonly in uranium/vanadium rich sandstones
- Found in carbon rich deposits including coal, oil shale, crude oil and tar sands

Annual World Production 2018

	mt/Year	$/mt
Steel	**1,800,000,000**	**$550**
Aluminum	**64,000,000**	**$2,400**
Copper	**10,000,000**	**$7,200**
Nickel	**2,300,000**	**$28,000**
Molybdenum	**264,000**	**$71,600**
Vanadium	**54,000**	**$65,000**

Vanadium Uses

Construction

Aerospace

Oil and Gas Pipelines

Vanadium Redox Flow Battery (VRFB)

Anti-Seismic Rebars

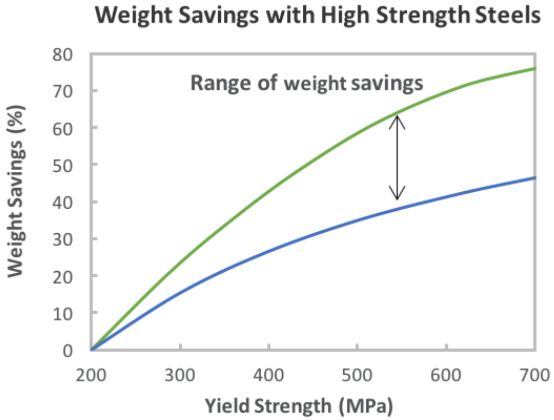
Bridges

Automotive

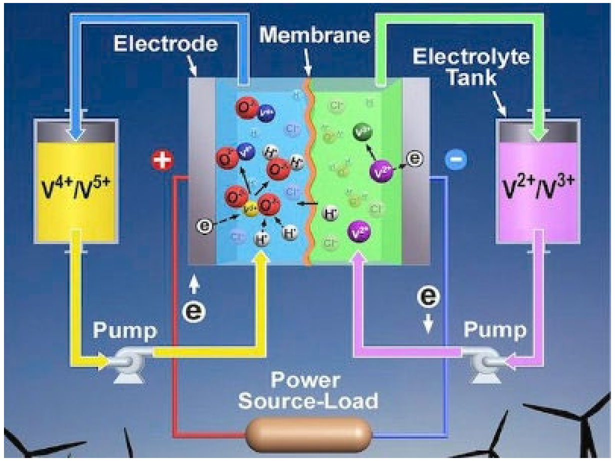
Wind Turbines

Environmental Benefits of Vanadium

- Less Steel
  - High strength vanadium steel enables you to use less steel
  - This can allow for a ~20% cost saving versus standard non vanadium quench and tempered steels
  - Additionally removing tempering steps saves significant energy and GHG emissions in production
- Lower emissions
  - Use of lightweight steels in vehicles and aerospace alloys in aircraft saves gasoline and jet fuel
- Energy Efficient Vanadium Redox Flow Battery (VRFB)
  - Deployed alongside renewables such as solar or wind, the VRFB makes interruptible renewable sources into reliable energy delivery methods



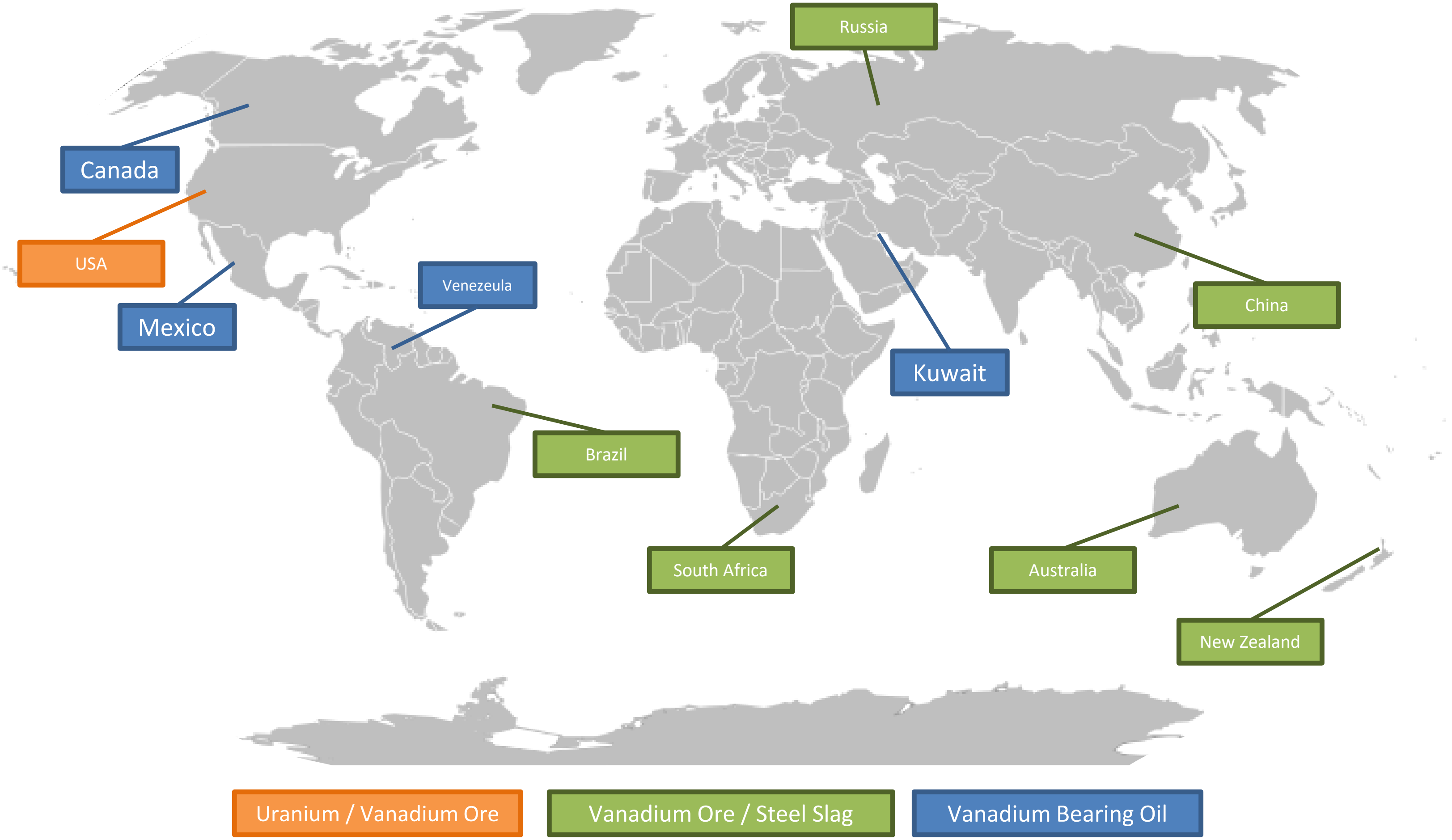
Ref. Michael Korchynsky, A new role for microalloyed steels-adding economic value, Proceedings of the 9th International Ferro Alloy Conference Infacon. Vol. 9. sn, 2001.



Strategic Importance of Vanadium

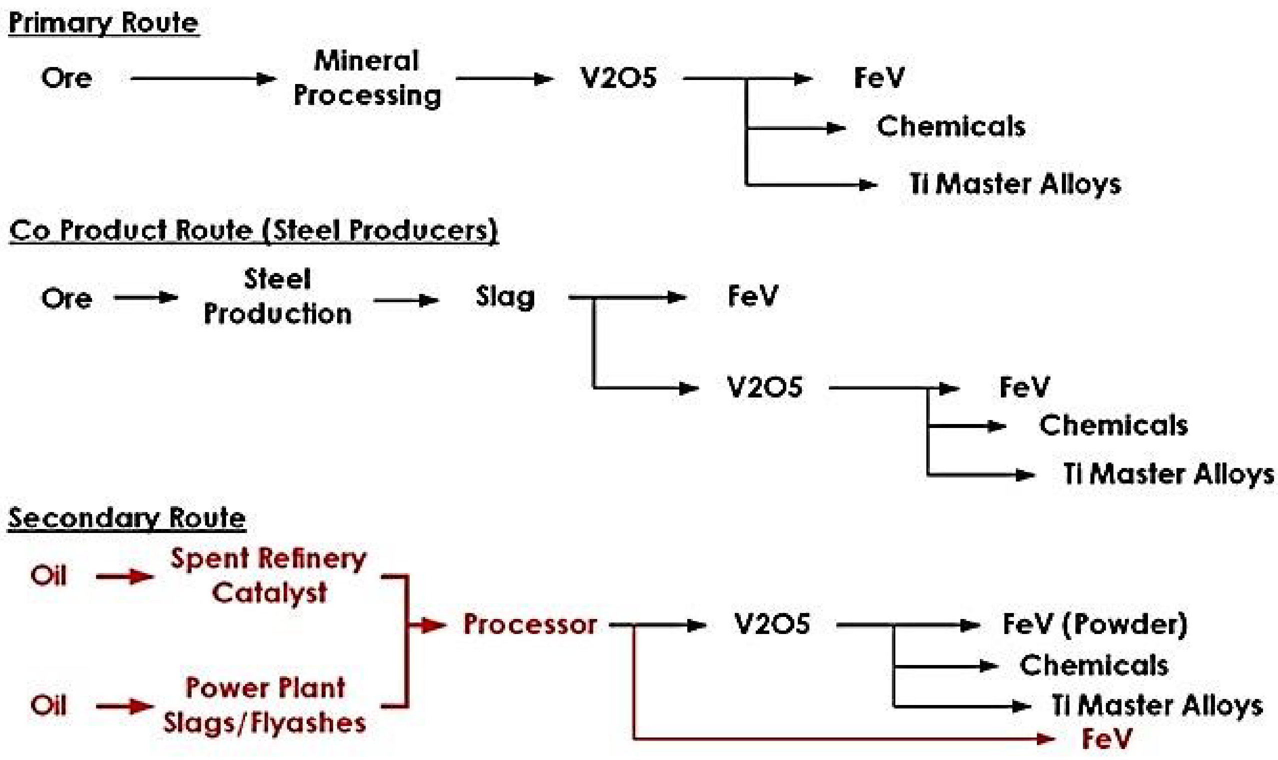
- May 2018 Vanadium named a US “Critical Mineral”
- “Vital to national security and economic prosperity”
- “Absence would have significant consequences for US economy and national security”
- Only 1 V_2O_5 and 1 high purity producer left in US
- FeV used in high-strength steels – 40% weight saving
- High purity vanadium alloyed with titanium for jet engines and aircraft
- US DoD Vanadium Technology Partnership Research
- No domestically available sufficient substitute for Vanadium exists
- Vanadium deposits mostly in Russia, China, SA & Brazil

World Vanadium Production Sources

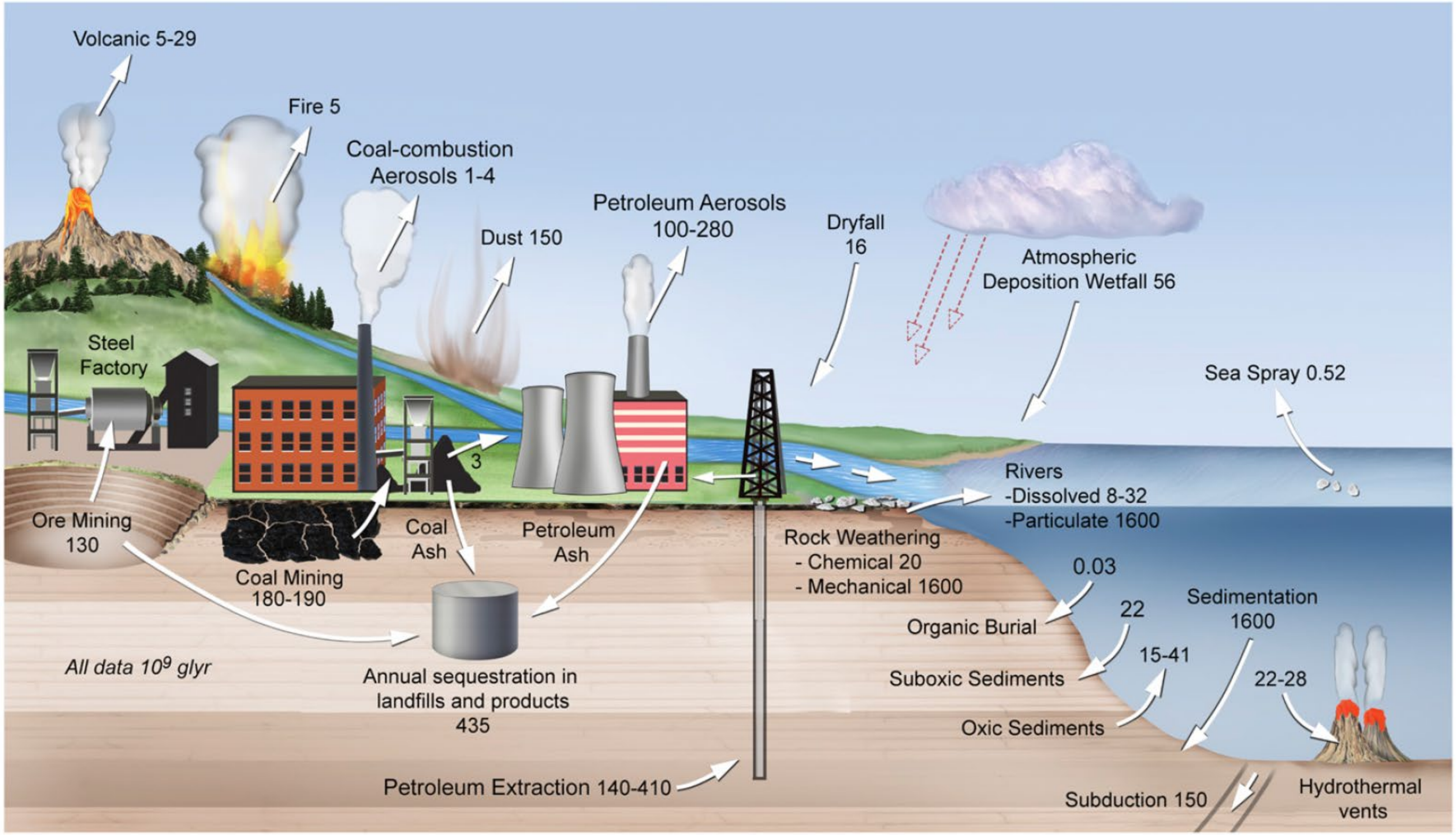


Vanadium Producers & Reclaimers Association

Vanadium Production Methodologies



Global Biogeochemical Cycle of Vanadium



Schlesinger, W.H., Klein, E.M., Vengosh, A., 2017. Global biogeochemical cycle of vanadium. Proc. Natl. Acad. Sci. Unit. States Am. 114, E11092–E11100.

All values in thousand metric tons of vanadium per year

Vanadium Oxidation States

Common Oxidations States

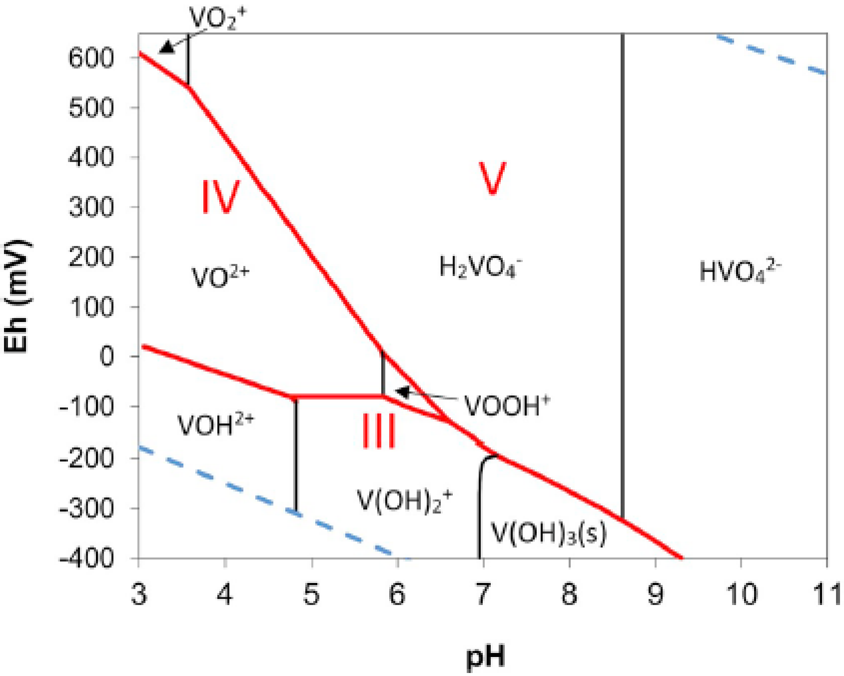
+5 - Yellow

+4 - Blue

+3 - Green

+2 - Violet

0 - Metal



Predominance diagram showing vanadium speciation as a function of acidity (pH) and redox potential (Eh) at 1µmol/l. Red lines separate predominance fields and dashed blue lines show stability with respect to H_2 (low Eh) and O_2 (high Eh)

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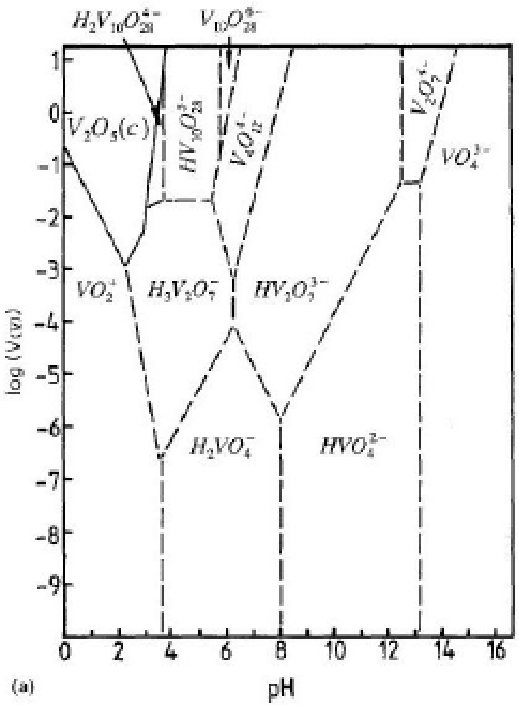
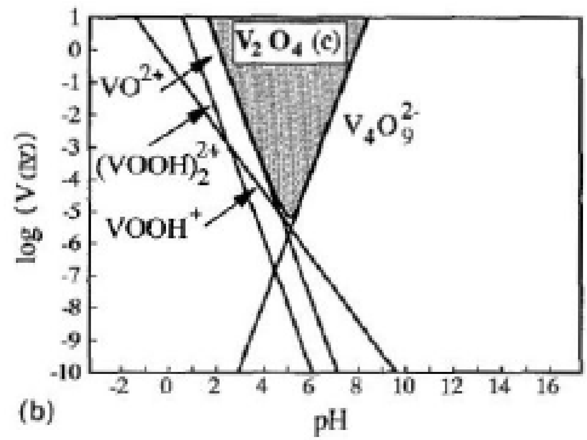
Chemistry of Vanadium +5 and +4



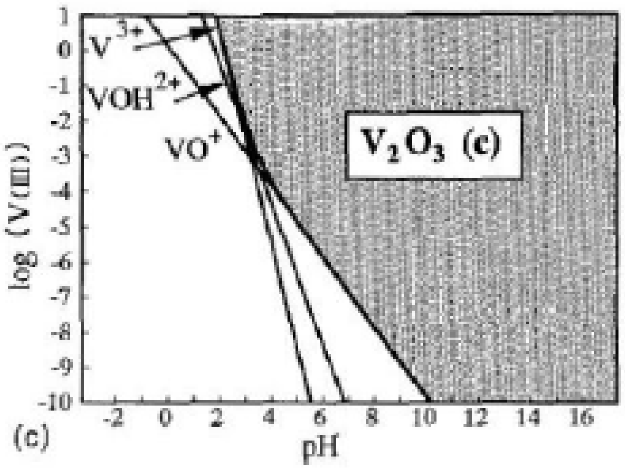
Oxidation State +5, Solid Phase is V_2O_5



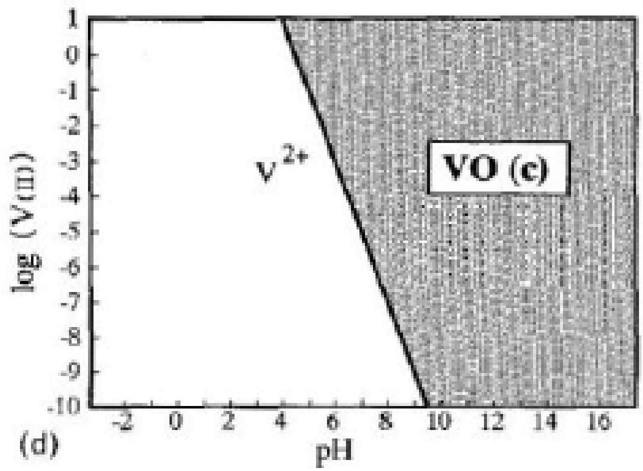
Oxidation State +4, Solid Phase is V_2O_4

- Aqueous chemistry of vanadium +5 is particularly complex depending on vanadium concentration and pH – total of 12 species and 8 charges from +1 to -6
- Aqueous chemistry of vanadium +4 remains complex but less so covering 5 species and 4 charges fro +2 to -2
- Ability of vanadium +5 and +4 to form both cationic and anionic species is important

Chemistry of Vanadium +3 and +2



Oxidation State +3, Solid Phase is V_2O_3



Oxidation State +2, Solid Phase is V_2O_4

- Aqueous chemistry of vanadium +3 remains complex but less so covering 4 species and 4 charges from +3 to 0
- Aqueous chemistry of vanadium +2 is simple
- Vanadium +2 is highly reactive and easily oxidized meaning it is unobserved in the environment

In Total

4 Oxidation States 23 Species 9 charges

Aqueous Vanadium Speciation

- As predicted from chemistry considerations oxidation states +4 and +5 are predominant in aqueous environmental samples
- Speciation can be challenging, especially at low environmental concentrations
- Utilize spectroscopy or chromatography methods developed in the last 20 years, for example:

Material Studied	Comment	Reference
Italian V rich waters	Chromatography, 40 % V +4	Minelli et al (2000)
Long Island Sound	Chromatography, 85% V+5, 15 % V +4, rising to 40% in spring	Wang et al (2009)
Forest acid soil extract	Chromatography (HPLC - ICP MS), predominance of V +4	Larsson et al (2015b)
Bottled mineral waters	Chromatography, predominance of V +5	Aureli et al (2008)
Sierra Nevada Groundwater	Chromatography, predominance of V +5	Gamage et al (2010)

Wang, D., Sañudo Wilhelmy, S.A., 2009. Vanadium speciation and cycling in coastal waters. Mar. Chem. 117, 52–58.
Minelli, L., Veschetti, E., Giammanco, S., Mancini, G., Ottaviani, M., 2000. Vanadium in Italian waters: monitoring and speciation of V(IV) and V(V). Microchem. J. 67, 83–90.
Larsson, M.A., D'Amato, M., Cubadda, F., Raggi, A., Oborn, I., Kleja, D.B., Gustafsson, J.P., 2015b. Long-term fate and transformations of vanadium in a pine forest soil with added converter lime. Geoderma 259–260, 271–278.
Gamage, S.V., Hodge, V.F., Cizdziel, J.V., Lindley, K., 2010. Determination of vanadium (IV) and (V) in Southern Nevada groundwater by ion chromatography-inductively coupled plasma mass spectrometry. Open Chem. Biomed. Methods J. 3, 10–17.
Aureli, F., Ciardullo, S., Pagano, M., Raggi, A., Cubadda, F., 2008. Speciation of vanadium (IV) and (V) in mineral water by anion exchange liquid chromatography-inductively coupled plasma mass spectrometry after EDTA complexation. J. Anal. At. Spectrom. 23, 1009–1016.

Solid State Vanadium Speciation

- Three oxidation states (+3, +4 and +5) are environmentally stable
- Speciation in the Solid State is challenging
- Direct measurement utilizes X-ray Absorption Near Edge Structure (XANES) Spectroscopy. Relatively few examples, most from the last decade.
- Can be used to identify single phases or model mixtures of oxidation states in more complex samples

Solid State Vanadium Speciation

Material Studied	Comment	Reference
Soils (n=12)	Range of mean oxidation state 3.7 to 4.6	Larsson et al (2015)
Soils (n=20)	Range of mean oxidation state 3.7 to 4.9	Larsson et al (2017)
Black Shales	Predominance of V +3 in all samples	Sahoo (2015)
Titanomagnetite	90% V +3 and 10% V +4	Balan et al (2006)
Blast Furnace Slags	Range of mean oxidation state 3.0 to 3.2	Larsson et al (2015)
Marine Sediment	Mean oxidation state 3.5	Bennett et al (2018)
River Reservoir Sediment	74% V +3 (V2O3 type phase) and 26% V +4	Nedrich et al (2018)
Water Pipe Scale	Vanadite (Pb/V) V +5	Gerke et al (2010)

Larsson, M.A., Baken, S., Smolders, E., Cubadda, F., Gustafsson, J.P., 2015a Vanadium bioavailability in soils amended with blast furnace slag. J. Hazard Mater. 296, 158–165.

Larsson, M.A., Hadialhejazi, G., Gustafsson, J.P., 2017a Vanadium sorption by mineral soils: development of a predictive model. Chemosphere 168, 925–932.

Larsson, M.A., et al., 2015b. Long-term fate and transformations of vanadium in a pine forest soil with added converter lime. Geoderma 259–260, 271–278.

Sahoo, S.K., 2015. Ediacaran ocean redox evolution. PhD Thesis. University of Nevada, Las Vegas, NV, USA.

Balan, E., et al., 2006. The oxidation state of vanadium in titanomagnetite from layered basic intrusions. Am. Mineral. 91, 953–956.

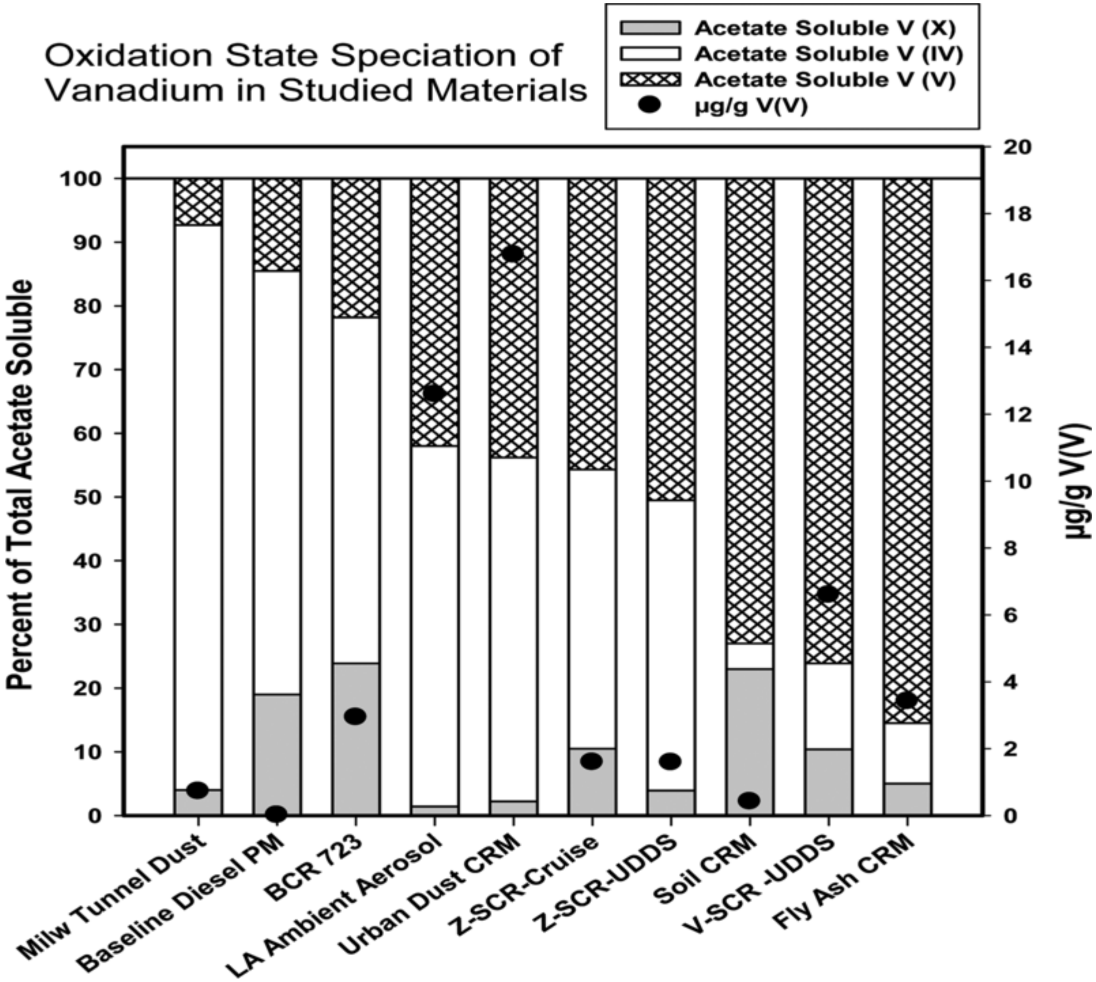
Nedrich, S.M., et al., 2018. Biogeochemical controls on the speciation and aquatic toxicity of vanadium and other metals in sediments from a river reservoir. Sci. Total Environ. 612, 313–320.

Bennett, et al., 2018. Synchrotron X-ray spectroscopy for investigating vanadium speciation in marine sediment. Limitations and opportunities. J. Anal. At. Spectrom.33, 1689–1699.

Gerke, T.L., Scheckel, K.G., Schock, M.R., 2009. Identification and distribution of vanadinite (Pb5(V5+O4)3Cl) in lead pipe corrosion by-products. Environ. Sci. Technol. 43, 4412–4418.

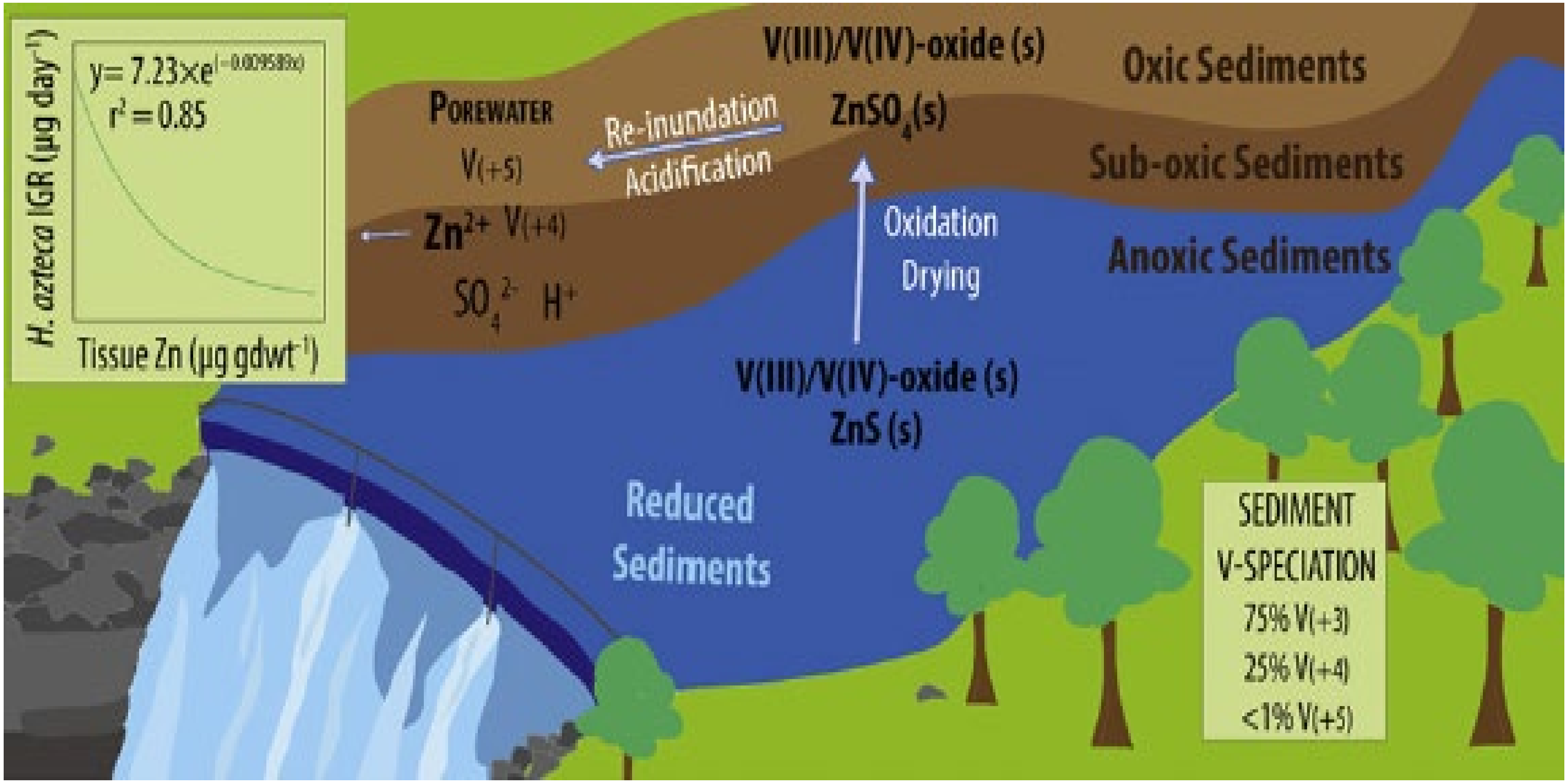
Ambient Air Vanadium Speciation

- Chemical Speciation of Vanadium in Particulate Matter Emitted from Diesel Vehicles and Urban Atmospheric Aerosols
- Typically mixtures of V +4 and V +5
- Vanadium +5 more dominant in finer fractions and V +4 more dominant in coarser materials
- Some evidence of V +3



Shafer, M.M., Toner, B.M., Overdier, J.T., Schauer, J.J., Fakra, S.C., Hu, S., Herner, J.D.,Ayala, A., 2012. Chemical speciation of vanadium in particulate matter emitted from diesel vehicles and urban atmospheric aerosols. Environ. Sci. Technol. 46, 189–195.

Vanadium in Sediments



Nedrich, S.M., Chappaz, A., Hudson, M.L., Brown, S.S., Burton jr., A., 2018. Biogeochemical controls on the speciation and aquatic toxicity of vanadium and other metals in sediments from a river reservoir. Sci. Total Environ. 612, 313–320.

Implications for Risk Assessment

- The form of vanadium has a significant impact on toxicity

- The acute inhalation toxicity of vanadium compounds in rodents was different depending on the oxidation state, solubility of vanadium and species tested

Rajendran N, Seagrave JC, Plunkett LM, MacGregor JA. 2016. A comparative assessment of the acute inhalation toxicity of vanadium compounds. Inhalation Toxicology 28:618-628. Epub 2016 Oct 6.

- A study by the National Toxicology Program demonstrated toxic effects on the lung from inhalation exposure to V_2O_5 particulate, whereas the form of vanadium systemically circulating was not toxic

National Toxicology Program (NTP). 2002. NTP Technical Report on the Toxicology and Carcinogenicity Studies of Vanadium Pentoxide (CAS NO. 1314-62-1) in F344/N Rats and B6C3F1 Mice (Inhalation Studies). National Toxicology Program, Research Triangle Park NC. NTP TR 507, NIH Publication No. 03-4441, pp. 352, dated December 2002

Summary

- Anthropogenic additions of vanadium to the environment comes primarily from the processing and burning of fossil fuels.
- Vanadium production has a small affect, and two routes actually sequester vanadium from byproducts (steel slags and petroleum wastes).
- Direct vanadium ore mining and processing is relatively small
- Vanadium chemistry is complex and characterized by equilibrium mixtures of oxidation states and species
- Much toxicological research focuses on V +5 but a review of evidence suggests this is not directly aligned to the predominant environmental forms

Research Needs

- The literature on environmental forms of vanadium, especially those associated with fossil fuel burning emissions is sparse. Additional work is required in this area using recently developed methods.

Thank you for your attention!