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VANADIUM BOOM DRIVING REVIVAL OF BY-PRODUCT VANADIUM RECOVERY FROM URANIUM ORES

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ABSTRACT

The vanadium price has been extremely volatile in recent years. After peaking in 2018, the price has declined due mainly to lower than expected demand in China attributed to the slow rate of compliance with China's new rebar standard for structural steel together with substitution with niobium. Another driver is the projected growth in the application of Vanadium Redox Flow Batteries for stationary energy storage for renewable power generation and electric vehicles (EVs) which could result in a long-term increase in demand and price.

The top four producing countries are China, South Africa, Russia, and Brazil from titaniferous magnetite ores. Typically the process comprises crushing, milling, magnetic separation, roasting, leaching, purification, precipitation, and calcining to produce V_2O_5 . Most of the V_2O_5 is converted into ferrovanadium or nitrogen vanadium alloy which are used as additives to strengthen steel. Other uses include catalysts such as in sulphuric acid converters.

Vanadium has been previously produced as a by-product from the processing of carnotite uranium-vanadium sandstone ores in western USA. A number of existing uranium plants and developing projects are planning or evaluating vanadium production to take advantage of the projected higher demand.

The presentation outlines flowsheets used by previous commercial by-product vanadium operations and identifies developing projects.

Keywords: Vanadium, By-Product vanadium, Projects, Uranium processing, Carnotite, Redox flow batteries, Stationary energy storage.

Outline

- Vanadium Demand and Price Drivers
- Current Vanadium Production and Uses
- By-Product Vanadium Recovery Past and Present
- Uranium-Vanadium Minerals
- Recovery Processes for Carnotite Ores
- Current By-Product Vanadium Production
- Potential By-Product Vanadium Projects
- Conclusions and References

Vanadium Demand and Price Drivers

- The vanadium price peaked in 2018 due to China's new rebar standard for structural steel, and the projected long term-growth of Vanadium Redox Flow Batteries for Evs and stationary energy storage for renewable power generation.
- However, the price has since declined due to the slow rate of compliance with China's new rebar standard, the substitution with niobium and the global slowdown caused by COVID 19.



⁽Ref: Origin Energy Website, accessed 18 April 2018)



(Ref: Bloomberg New Energy Finance Website, accessed 18 April 2018)

Current Vanadium Production and Uses

- The top four producing countries are China, South Africa, Russia, and Brazil from titaniferous magnetite ores.
- Typically the process comprises crushing, milling, magnetic separation, roasting, leaching, purification, precipitation, and calcining to produce V₂O₅.
- Most of the V₂O₅ is converted into ferrovanadium or nitrogen vanadium alloy which are used as additives to strengthen steel.
- Other uses include catalysts such as in sulphuric acid converters.

By-Product Vanadium Recovery Past and Present

- In the 1950s-70s, vanadium was commonly produced as a by-product to uranium from the processing of carnotite bearing sandstone ores especially in some western USA states.
- Currently, a number of existing uranium plants and developing projects are planning or evaluating by-product vanadium from carnotite bearing sandstone and calcrete ores to take advantage of the projected boom in demand for batteries.

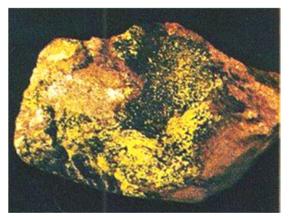
Uranium-Vanadium Minerals

Most important uranium-vanadium minerals:

carnotite $K_2(UO_2)_2(VO_4)_2 \cdot 1-3H_2O$ tyuyamunite $Ca(UO_2)_2V_2O_8 \cdot (5-8)H_2O$ metatyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot 3-5H_2O$

Less common minerals:

montroseite (V,Fe)O(OH) paramontroseite (VO₂)



Carnotite

Recovery Processes for Carnotite Ores

Salt Roasting/Acid Leaching of Sandstone Ores

Was operated in the western USA up to the 1970s. The typical flow sheet was:

- Multiple hearth roasting at 825-850°C for 1-2 hours of dry ground ore at 1.7 mm mixed with 6-10% NaCl which renders 70-80% of vanadium water soluble. Oxidation was used to ensure V was pentavalent and U hexavalent for down stream processing.
- Calcine was quenched with water to extract water-soluble sodium vanadate, followed by solid/liquid separation and vanadium recovery from the solution by precipitation or SX.
- The solids were agitated leached with dilute sulphuric acid for uranium and additional vanadium followed by solid/liquid separation. Uranium was recovered from solution by SX (or IX), then vanadium by precipitation.

Recovery Processes for Carnotite Ores (Cont.)

High Temperature Acid Leaching of Sandstone Ores

Tended to replace salt roasting in the USA from 1970s. The typical flow sheet was:

- Agitated acid leaching of wet ground ore at 80 90°C to solubilize uranium and vanadium followed by solid/liquid separation.
- Recovery of uranium from solution by SX which rejects the tetravalent vanadium.
- Vanadium was extracted from the USX raffinate by a second SX after conversion to pentavalent by raising the pH, then recovered by precipitation.

Recovery Processes for Carnotite Ores (Cont.)

Alkaline Leaching of Calcrete Ores

In more recent years, projects have been proposed in Namibia, Australia and Mauritania. The typical flowsheet is:

- Upgrading by scrubbing and classification.
- Agitated alkaline leaching of the fine fraction at 60 70°C to solubilize uranium and vanadium, followed by solid/liquid separation.
- May include pre-heating/heat recovery.
- Solid/liquid separation.
- Uranium recovery from solution by IX which rejects the vanadium.
- Vanadium recovery of from IX barren solution by precipitation.

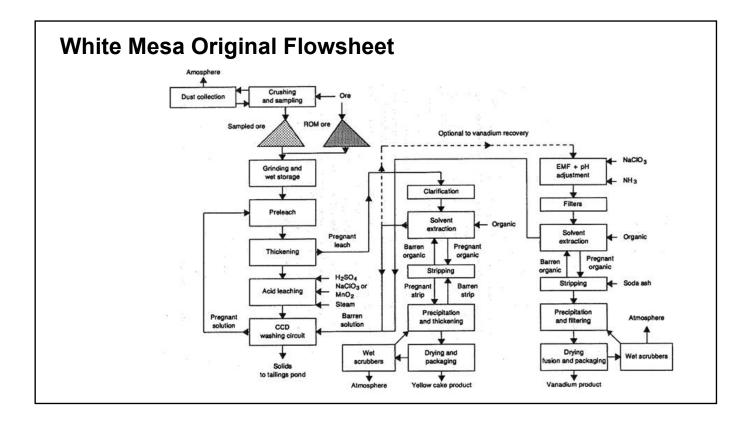
Current By-Product Vanadium Production

White Mesa, Energy Fuels Nuclear, Utah, USA: sandstone ore, carnotite mineralization, sulphuric acid leach.

- Operated 1980-1997 by Energy Fuels Nuclear them re-started in 2008 by Denison Mines of Canada and acquired by Energy Fuels in 2012.
- Uranium circuit restarted in 2018 and vanadium by-product recovery in January 2019, initially from existing pond solutions and later to treat U/V ores with high vanadium content.
- Currently undertaking studies for recovering uranium and a REE concentrate from ores supplied by other mining companies. (Ref: Mining News Digest, Mining.Com, 28 June 2020)

Original White Mesa Flowsheet

- 2-stage leaching in which second stage used strong sulphuric acid at 75°C to maximize uranium and vanadium recovery (95% and 75% respectively).
- Included two SX circuits in series for uranium then vanadium. (Vanadium s in the tetravalent form in the PLS and is not extracted in USX.)
- USX used conventional tertiary amine extraction. Strip used acidified sodium chloride due to presence of molybdenum, then precipitation with ammonia, dewatering and calcination to oxide at 590°C.
- VSX also used tertiary amine after the pH of the USX raffinate was raised with ammonia and sodium chlorate to change vanadium to pentavalent. Strip used soda ash followed by precipitation with ammonium sulphate, then calcination to oxide at 450°C, fusion at 900°C and cooling on a casting wheel.



Potential By-Product Vanadium Projects

- Langer Heinrich, Paladin Energy, Namibia: surficial calcrete ore, carnotite, alkaline leach. Operation suspended due to low U prices. New flowsheet studied based on in-house testwork in 2019 involving vanadium recovery. (Ref: Paladin website accessed 13 December 2018)
- Tiris, Mauritania, Aura Energy, surficial calcrete ore, carnotite mineralisation, alkaline leach. DFS for uranium production completed 2019. Potential for vanadium production.

(Reference Aura website, accessed 21 September 2020)

Potential By-Product Vanadium Projects (Cont.)

- Wiluna, Western Australia, Toro Energy, surficial calcrete ore, carnotite mineralisation, alkaline leach. Undertaking leach optimization and IX testwork for vanadium by-product recovery to add project value. (Ref. Toro website accessed 8 April 2019)
- Amarillo Grande, Argentina, Blue Sky Uranium, surficial sandstones and conglomerates ore, carnotite mineralization with lesser tyuyamunite, leibigite, and an unidentified uranium-bearing mineral species. Alkaline leach, uranium and vanadium to be separated by selective chemical precipitation, uranium solids then calcined to U₃O₈ or UO₃ and vanadium solids calcined to V₂O₅. Preliminary economic assessment including testwork.

(Ref: Blue Sky website, accessed 8 April 2019)

Potential By-Product Vanadium Projects (Cont.)

 Yeelirrie, Western Australia, Cameco, surficial calcrete ore, carnotite mineralisation, alkaline leach. Project is on hold till more favourable uranium market conditions. Vanadium recovery has been evaluated and rejected to date as uneconomic and potential environmental impacts. (Ref. Yeelirrie Uranium Project, Public Environmental Review, EPA WA website, accessed 8 April 2019)

Note: No announcement to revisit V recovery has been sighted.

Conclusions

- By-product vanadium recovery is commercially proven for carnotite bearing sandstone ores and successfully tested for calcrete ores.
- Salt roasting technology was commonly applied to sandstone ores in the USA up till the 1970s.
- Salt roasting tended to be replaced by high temperature acid leaching in the USA from the 1970s.
- The only current operation known to the presenter is White Mesa in Utah, USA. It processed sandstone ore by high temperature acid leaching during 1980-1997. Current owners Energy Fuels restarted uranium production in 2018 and vanadium in 2019.
- A number of current projects have the potential for by-product vanadium via alkaline leaching of carnotite bearing calcrete ores.

References

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- Uranium Extraction Technology, Technical Support Series No. 3590, IAEA, Vienna, 1993