CHAPTER 12.42

Vanadium

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Vanadium is commercially produced around the world from a variety of feedstocks. These include vanadium ores, vanadium slag concentrates, boiler and fly-ash residues from power-generation plants, vanadium cokes from oil refining, and spent catalysts from chemical processing and oil refining. Approximately 85% of worldwide vanadium production is from titaniferous magnetite ore, either as primary production from magnetic concentrate recovered from the ore, or as co-production from vanadium-bearing steel slag produced during steelmaking operations utilizing the ore. Approximately 91% of worldwide vanadium production is consumed by the steelmaking industry to achieve strength and hardness requirements in various steel grades. The remaining 10% is consumed in the production of high-strength titanium alloys, catalysts for manufacturing chemicals, catalysts for the removal of sulfur dioxide (SO_2) and nitrogen oxide (NO_x), and energy storage batteries.

The processing of vanadium, regardless of feedstock source, utilizes common industry metallurgical extraction and chemical unit operations. These include comminution; physical concentration, involving magnetic or gravitational separation; vanadium dissolution by common alkaline or acid fluxes or leachates; chemical separation for purification by selective precipitation and ion exchange or solvent extraction; vanadium precipitation and crystallization; and filtration, drying, and calcining.

Commodity-grade vanadium pentoxide (V_2O_5), used to produce ferrovanadium (FeV) for the steel industry, has a purity level of +96% V_2O_5, whereas chemical-grade material has a purity level of +99.5% V_2O_5. High-purity V_2O_5 (+99.5%) production generally requires solvent extraction or ion exchange, followed by crystallization to achieve the purity requirements, although commodity-grade material can be produced using only selective precipitation.

This chapter primarily focuses on the processing of commodity-grade vanadium, predominantly from titaniferous magnetite ores and steel slag concentrates.

EXTRACTION VIA SALT ROAST–WATER LEACH

Regardless of whether the raw material is slag or vanadium-containing ore, the basic extraction process for recovering vanadium is similar, involving a salt roast–water leach route (McRae et al. 1969; Gupta and Krishnamurthy 1992; Goddard and Fox 1980). Typically, vanadium in titaniferous magnetite concentrate is in a reduced state. To improve its solubility, the vanadium needs to be oxidized to the pentavalent state to form sodium metavanadate. The oxidation is performed in a rotary kiln.

The key to successful vanadium recovery from titaniferous magnetite involves not only the oxidation of vanadium but also the oxidation of magnetite to hematite. When magnetite is oxidized to hematite, the accessibility of oxygen and sodium salt to react with vanadium in the titaniferous magnetite concentrate improves because of the increase in porosity. This process liberates vanadium from the spinel structure.

Sodium chloride, sodium carbonate, sodium sulfate, and/or a mixture of these have been widely applied as flux. Sodium oxalate has been used as flux at the Windimurra operation in Australia. In Russia, lime has been used as flux in the roasting reaction. With sodium salts, the roasted product is leached in water. Lime, however, requires acid leaching to promote the solubility of vanadium.

Sodium chloride fluxing requires the presence of water vapor or oxygen to drive the formation of sodium metavanadate. The reaction is represented by the following:

$$2NaCl + O_2 + H_2O + V_2O_3 = 2NaVO_3 + 2HCl(g) \quad \textbf{(EQ 1)}$$

or

$$2NaCl + 3/2O_2 + V_2O_3 = 2NaVO_3 + Cl_2(g) \quad \textbf{(EQ 2)}$$

If the vanadium is in the pentavalent state, the reaction is

$$2NaCl + V_2O_5 + H_2O = 2NaVO_3 + 2HCl(g) \quad \textbf{(EQ 3)}$$

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Under prolonged roasting, sodium pyrovanadate ($Na_4V_2O_7$) can form (Goddard and Fox 1980). Sodium pyrovanadate is relatively water soluble, but its formation is unnecessary as it consumes more salt. The mechanisms of sodium pyrovanadate formation are as follows:

$$2NaCl + 3/2O_2(g) + V_2O_3 = 2NaVO_3 + Cl_2(g) \quad \textbf{(EQ 4)}$$

$$2NaCl + H_2O(g) + 2NaVO_3 = Na_4V_2O_7 + 2HCl(g) \quad \textbf{(EQ 5)}$$

Insufficient salt and/or water vapor in the reaction with sodium chloride can lead to water-insoluble vanadates called *bronzes*, with a sodium-to-vanadium mole ratio of less than 1.

Use of sodium sulfate flux is reported to produce superior vanadium recovery over sodium chloride. As opposed to sodium chloride, the reaction requires no water vapor or oxygen to trigger the formation of sodium metavanadate. In fact, sulfur trioxide (SO_3), an oxygen supplier, is generated when sodium sulfate decomposes at high temperature through the equilibrium reaction of $SO_3 = SO_2 + ½O_2$.

Sodium carbonate roasting has been repeatedly reported to generate the best vanadium water leach recoveries from titaniferous magnetite when compared with sodium sulfate or sodium chloride. This is mainly related to the alkaline character of sodium carbonate, which has been reported to be more aggressive in the attack of the magnetite spinel as compared to sodium chloride or sodium sulfate. However, for this same reason, it has been found to be less selective than sodium chloride or sodium sulfate. When sodium carbonate is used, the presence of an oxidizing environment is critical. Free oxygen content of 4% is required to maintain a good oxidizing environment.

Sodium oxalate found its application in salt roasting at the Windimurra operation because of the availability of a low-cost waste resource. Sodium oxalate decomposes to sodium carbonate on heat treatment. The reaction mechanism with sodium oxalate is shown in the following equations:

$$Na_2C_2O_4 = 2Na_2CO_3 + CO \quad \textbf{(EQ 6)}$$

$$V_2O_5 + Na_2CO_3 = 2NaVO_3 + CO_2 \quad \textbf{(EQ 7)}$$

The proportion of vanadium recoverable from a salt roasting operation usually ranges from 70% to 90%. Most of the problems in the recovery arise from side reactions of sodium compounds with other constituents in the ore. These constituents include silica and silicates; claylike complexes of calcium, aluminum silicate, gypsum, calcium carbonates, iron oxides; and also organic matter.

The high silica and lime content in vanadium-bearing materials is the main cause of unproductive side reactions in salt roasting. The detrimental effect of siliceous materials is caused by the formation of low-melting sodium iron silicate-acmite ($Na_2O{\cdot}Fe_2O_3{\cdot}4SiO_2$) that retains vanadium oxide in a water-insoluble solid solution. Its formation can retard magnetite oxidation by fusing. Goddard and Fox (1980) found that vanadium extraction drops below 20% from magnetite with 7.5% silicon dioxide (SiO_2) or more. At Windimurra, the vanadium extraction dropped to 70% when the titaniferous magnetite concentrate contained approximately 4.6% SiO_2, but increased to 88% as the silica content reduced to 2.7% SiO_2.

Silica is a sodium salt consumer. Silica is typically rejected by magnetic separation in the concentrator plant. Alternatively, alumina can be added to form sodium aluminum silicates with higher melting temperature. This suppresses the competing effect from silica for sodium salt in the roasting operation. However, its commercial application is unknown. Typically, the silica content should not be greater than 3% SiO_2. The rule of thumb is that the alumina-to-silica ratio should be greater than 1, or the combined silica and alumina content should be less than 5%.

The presence of lime can lead to the formation of water-insoluble calcium vanadate. This is particularly true when roasting with neutral salts such as sodium sulfate. Alkaline salts, such as sodium carbonate, tend to yield higher extraction of vanadium for ore containing high lime levels. Controlling the gangue minerals content along with the roasting conditions is important to maximize vanadium extraction.

PRODUCTION AND PROCESSING HISTORY

Vanadium was first discovered in 1801 by Andrés Manuel del Río, a Spanish mineralogist, in a brown lead sample collected from a mine near Hidalgo, Mexico, but it was mistaken as a form of chromium (Hilliard 1997). In 1830, Nils Gabriel Sefström, a Swedish chemist, rediscovered vanadium in a converter slag produced from an iron ore sample in Taberg, Sweden, and named it vanadium, in honor of the Scandinavian goddess of beauty, Vanadis. Then in 1868, Henry Roscoe successfully produced vanadium metal from vanadium chloride by reducing it in hydrogen.

In the early 1870s, the high cost and scarcity of vanadium restricted its commercial potential. Nevertheless, extensive studies were carried out to investigate the suitability of vanadium as an alloying agent for steel (Duke 1983). Commercial application of vanadium as an alloying agent for steel started in 1905 when Henry Ford recognized its benefits for use in the automobile industry. Later, in 1960, vanadium found its application in titanium alloys for jet engines and airframes.

China, South Africa, and Russia are the largest global producers, supplying approximately 90% of the global vanadium demand in 2014. It is estimated that China supplies 55% of the global vanadium demand, and South Africa and Russia contribute 21% and 14%, respectively. World vanadium resources exceed 63 Mt (million metric tons) (Polyak 2013). Vanadium occurs in combination with more than 65 different minerals in deposits such as phosphate rock, titaniferous magnetite, and uraniferous sandstone and siltstone. Vanadium is also found in some crude oils in the form of organic complexes. This vanadium is concentrated in boiler slag and ash generated from the burning of oils in power stations. Vanadium is also concentrated in spent catalysts from oil refinery processing. These vanadium raw materials are classified as secondary material. The extraction of vanadium from secondary material equals 9% of global production (TZMI 2015).

Titaniferous magnetite ore accounts for ~85% of global vanadium resources (Vanitec 2014), making it the most important source of vanadium. In titaniferous magnetite ore, the titanium is mainly present as a solid solution in the titanium-rich magnetite phase (ulvöspinel [Fe_2TiO_4]) and to a lesser degree as ilmenite (Fischer 1975). The vanadium in the ore occurs as a solid solution within the magnetite-ulvöspinel, where V^{3+} substitutes Fe^{3+} in the magnetite crystal lattice.

Early Production

The change in the supply and commercial value of vanadium started with the discovery of vanadium-bearing asphaltic deposits at Minas Ragra in Peru in 1905. American Vanadium Company began mining the deposits in 1907 (Anon. 1920; Hammond Swayne LLC 2015). The Minas Ragra deposit was the most productive single deposit of vanadium in history.

The vanadium mineralization was hosted within patronite, containing up to 24.8% V_2O_5. Maximum production of 2,074 t (metric tons) of V_2O_5 was recorded in 1920. By 1929, the high-grade vanadium ore was nearly exhausted. The mine was subsequently closed in 1930 but reopened in 1934 after a new process was developed to extract vanadium from low-grade ore (Gomi and Whetham 2012). It involved salt roasting and sulfuric acid leaching. The mine continued to operate until 1955 and produced a total of 39,009 t of V_2O_5 between 1907 and 1955 (Crabtree and Seidel 1961).

Significant mining activities for vanadium also took place in southwestern Colorado and southeastern Utah (United States). Roscoelite ore was mined exclusively for vanadium in Colorado near Placerville from 1910 to 1920 and then at Rifle Creek from 1925 to 1954 (Hammond 2013). Vanadium was also recovered from carnotite ore (containing both uranium and vanadium) in the Colorado Plateau, spanning Colorado, Utah, Arizona, and New Mexico in the United States. From 1946 to 1960, the Colorado Plateau supplied 55% of the world's recoverable vanadium pentoxide, producing a total of 47,428 t of V_2O_5 (Crabtree and Seidel 1961).

Salt roasting has been practiced in Colorado since 1910 (Crabtree and Seidel 1961). Carnotite ore is roasted with sodium chloride. Sodium chloride is added at a flux-to-ore ratio of 6–10 wt %. The mixture is roasted at 820°–850°C for 1–3 hours in a multiple-hearth roaster or rotary kiln. Vanadium extraction typically ranges from 70% to 80%. However, if the carnotite ore contains lime in excess of 6%, vanadium extraction can drop below 60% because of the formation of water-insoluble calcium vanadate. The roasted product is subsequently subjected to either alkaline or water leaching for vanadium recovery. When leached in water, the vanadium is selectively dissolved in solution and recovered by precipitation.

At the Newmire operation in Colorado, vanadium was precipitated as iron vanadate using ferrous sulfate. The iron vanadate was then reduced to ferrovanadium in an aluminothermic reactor (Crabtree and Seidel 1961). At the Rifle operation, the vanadium in solution was precipitated as sodium hexavanadate, commonly known as *red cake*.

The vanadium in solution is heated to 80°–90°C, and sulfuric acid is added to yield an optimum pH of 2.5–3.0 for the red cake formation. The reaction mechanism is as follows:

$$6NaVO_3 + 2H_2SO_4 = Na_2H_2V_6O_{17} + 2Na_2SO_4 \qquad \textbf{(EQ 8)}$$

The red cake is then fused into vanadium oxide. Typically, the fused oxide produced directly from red cake contains 88%–92% V_2O_5 with ~8% sodium oxide (Na_2O) as the principal contaminant.

When alkaline leaching is employed, both uranium and vanadium dissolve, requiring further treatment to separate uranium from vanadium. The leaching is performed using sodium carbonate, sodium bicarbonate, or sodium hydroxide solution as the lixiviant (Gupta and Krishnamurthy 1992). Alkaline leaching is attractive for feed material containing high amounts of lime, as insoluble calcium vanadate is converted to soluble sodium vanadate.

When acid or alkaline leaching is employed, the vanadium in solution is purified via either chemical separation, ion exchange, or solvent extraction. The chemical separation process is highly complex and was gradually phased out and replaced by ion exchange and/or solvent extraction. Solvent extraction and ion exchange are employed to recover vanadium from acidic solutions (Gupta and Krishnamurthy 1992; Crabtree and Seidel 1961).

At the Uravan operation in Colorado, Union Carbide Nuclear Company employed column ion exchange technology to separate uranium from vanadium. Any pentavalent vanadium in acid leach liquors was initially reduced to the quadrivalent state with sulfur dioxide. The uranium was loaded to the resin, while the vanadium passed through the columns. Vanadium recovered from ion exchange effluent was recovered by precipitation.

Solvent extraction technology was applied at the Grand Junction and Rifle operations for separating uranium from vanadium in acid leach liquors. The uranium in the acid leach liquors was loaded onto di-2-ethylhexyl phosphoric acid (DEHPA). The extractant loaded with uranium was stripped with 10% sodium carbonate solution. The vanadium in the raffinate was recovered by precipitation. At the Rifle operation, Union Carbide Nuclear Company adopted a similar solvent extraction technology to that used by Climax Uranium Company. However, the vanadium in raffinate, recovered from the uranium solvent extraction circuit, was subjected to purification by solvent extraction using DEHPA. The extractant loaded with vanadium was stripped with sulfuric acid. The generic processing route for vanadium extraction from carnotite ore is presented in Figure 1.

Apart from patronite, roscoelite, and carnotite, vanadium has also been recovered from descloizite ores as the principal metal. Descloizite ore was mined at Otavi Mountainland in Namibia. This mine was in operation from 1925 until 1978.

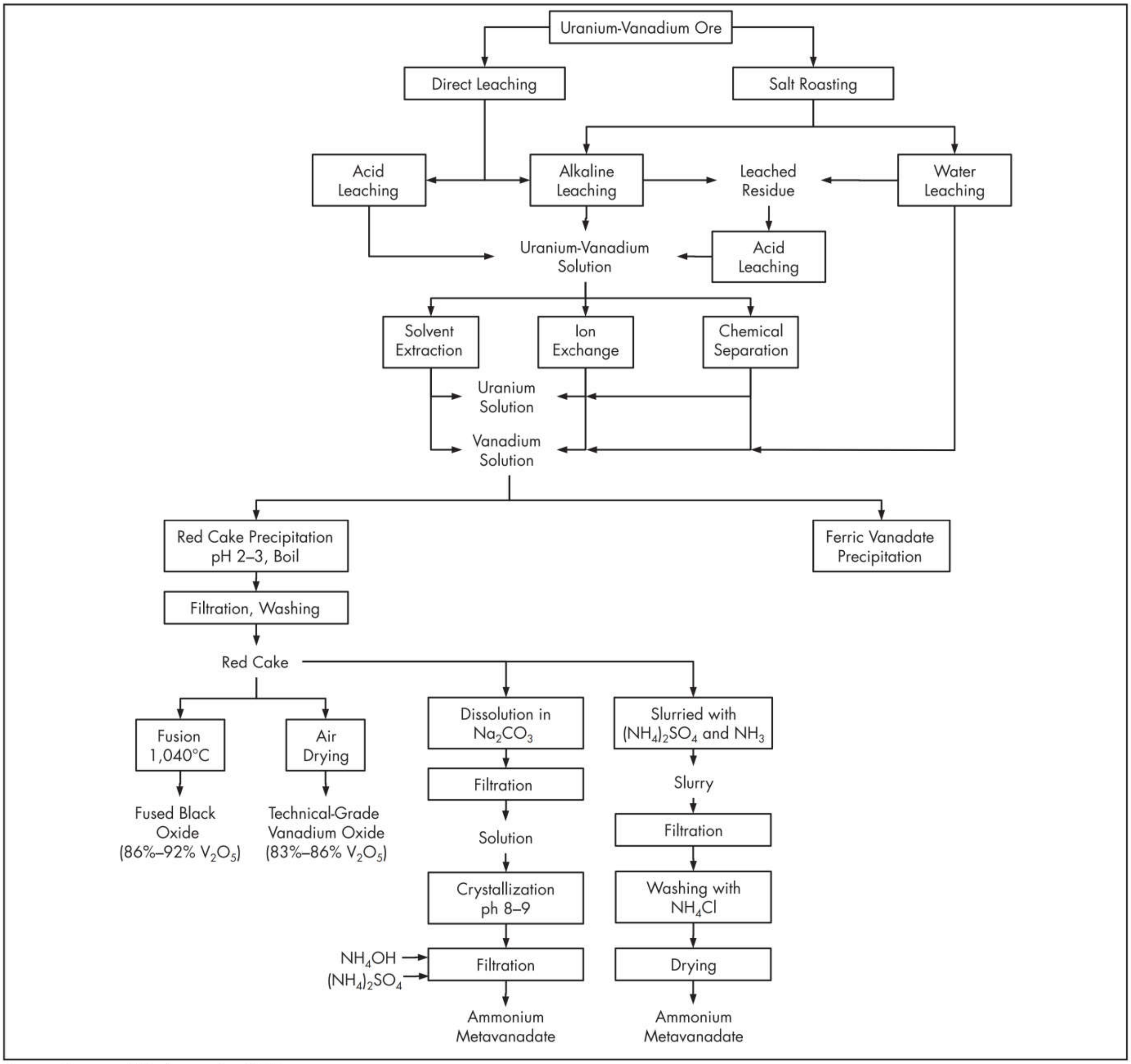
Vanadium Extraction from Titaniferous Magnetite

In the 1970s, titaniferous magnetite ore emerged as the most important source for vanadium, replacing carnotite ore. It was discovered that ~98% of globally known vanadium reserves are contained in titaniferous magnetite ore. Mining titaniferous magnetite ore for vanadium on a commercial scale began in Finland around 1953, and then in South Africa by 1957. Titaniferous magnetite ore was mined in the former Soviet Republic in the early 1960s. Then in the early 1970s, it was mined in large quantities in China.

This raw material can be processed directly for vanadium in primary production, or it can be recovered as a by-product from vanadium-bearing slag from the steelmaking industry. The latter is the most common processing method used by the key global vanadium producers. The generic process flow sheet for recovering vanadium from titaniferous magnetite ore is presented in Figure 2.

Finland

In Finland, titaniferous magnetite ore was sourced from the mines at Otanmaki and Mustavaara (Gupta and Krishnamurthy 1992). The operation at the Otanmaki mine started in 1953. The as-mined ore comprised a magnetite-ilmenite deposit hosting about 0.4% V_2O_5. The ore was physically beneficiated using magnetic separation, producing ilmenite and magnetite concentrates. The ilmenite concentrate was sold as a marketable titanium concentrate. The magnetite concentrate, which contained 1% V_2O_5, 60% Fe, and 2.2% titanium dioxide



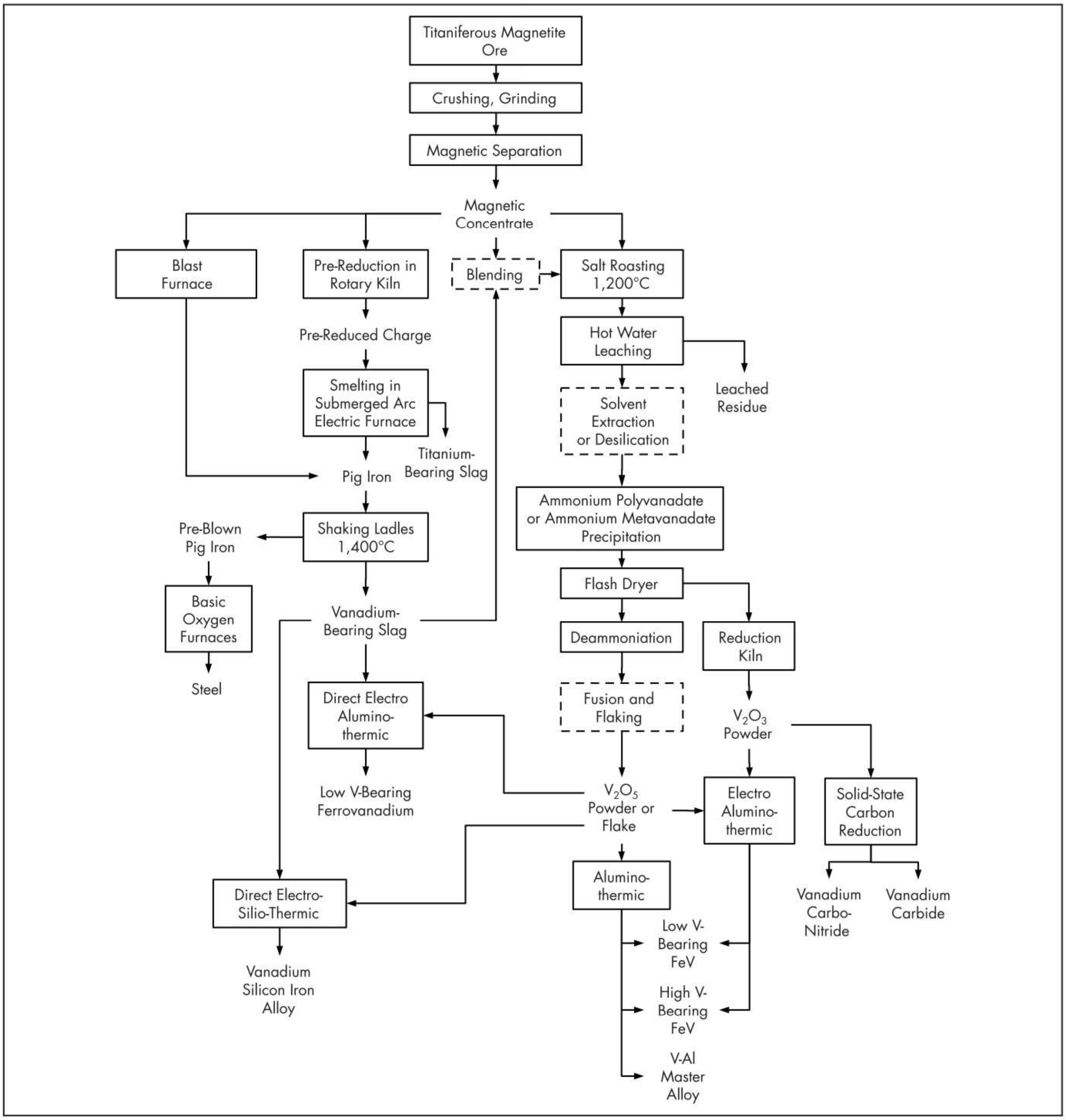
Source: Gupta and Krishnamurthy 1992

Figure 1 Extracting vanadium from uranium-vanadium ore

(TiO_2), was processed through a salt roast–water leach route for vanadium recovery.

Sodium sulfate was originally used as a sodium flux but was later replaced with sodium carbonate. The magnetite concentrate is mixed with sodium carbonate and pelletized in balling drums. The pellets are heated to 1,200°C in two parallel oil-fired shaft furnaces. The vanadium in the concentrate reacts with the sodium to form sodium metavanadate. Hot water is used to leach vanadium from the roasted pellets. Vanadium is precipitated from the liquor as ammonium polyvanadate. The ammonium polyvanadate is filtered, dried, decomposed, fused, and flaked to vanadium pentoxide. The leached pellets can be sold to steel producers as a high-grade concentrate.

The operation at Mustavaara mine began in 1976. The deposit was similar to the Otanmaki deposit except that the magnetite and ilmenite were finely disseminated. This made the separation of magnetite from ilmenite impossible. The vanadium grade in the feed ore was approximately 1.6% V_2O_5. Vanadium was recovered using the same salt roast–water leach route as that used at the Otanmaki operation, but it required a desilication process for silicate removal prior to precipitation. The leached residue contained high TiO_2 content and was unsuitable for smelting in a conventional blast furnace for steelmaking. The leached residue was therefore discarded into a tailings storage facility. The mine was closed in 1986. Since then, there has been no reported vanadium production in Finland.



Source: Gupta and Krishnamurthy 1992

Figure 2 Extracting vanadium from titaniferous magnetite ore

South Africa

Multiple vanadium production operations exist in South Africa.

Vantra. Minerals Engineering Corporation of South Africa, a subsidiary of Minerals Engineering of Colorado, commissioned a processing plant in 1957 at Kennedy Vale in Eastern Transvaal (Rohrmann 1985). Titaniferous magnetite ore from the Bushveld Complex was processed using a salt roast–water leach route.

In 1966, Anglo American acquired the company and it became known as the Vantra division of Highveld Steel and Vanadium Corporation. Kennedy Vale mine was the main ore supplier to Vantra up to 1972 (Rohrmann 1985). Thereafter, Mapochs mine became the principal supply source. The ore was processed through wet milling and upgraded by magnetic separation for rejection of gangue minerals. The magnetic concentrate contained 1.65% V_2O_5, 56.4% Fe, 14.1% TiO_2, 1.2% SiO_2, and 3.1% aluminum oxide (Al_2O_3).

The ore, mixed with sodium flux, was roasted either in multiple-hearth Skinner roasters or rotary kilns. The processing plant was comprised of four identical 10-hearth Skinner roasters (6.1 m in diameter), three small rotary kilns (1.52 m in diameter × 18.3 m long), and one larger rotary kiln (2.6 m in diameter × 36.5 m long).

Roasting was initially carried out in the Skinner roaster using sodium chloride. Sodium chloride is used because of its ability to selectively attack vanadium and its comparatively lower operating temperature of 800°–900°C. This process generates large amounts of hydrochloric acid. The hydrochloric acid is captured and converted to ammonium chloride in an ammonia solution. The process is inefficient and presents major pollution and corrosion problems, and it delivers lower vanadium conversion compared to roasting with sodium carbonate or sodium sulfate. After 1974, sodium carbonate, sodium sulfate, or a mixture of both, replaced sodium chloride.

The reaction with sodium sulfate was found to be highly selective in its attack on vanadium. It produces a higher-purity pregnant solution compared to sodium carbonate. Co-dissolution of sodium aluminate, chromate, and silicate, which was encountered in the roasting with sodium carbonate, was not observed.

Roasting with sodium carbonate requires a roasting temperature of 900°–1,200°C. For sodium sulfate, the effective roasting temperature needs to be higher than 1,200°C. At Vantra, the upper temperature limit of the Skinner roasters was lower than 1,200°C; thus, the Skinner roasters were unable to deliver the required temperature for maximum recovery of vanadium. This subsequently led to the installation of rotary kilns.

The hot calcined ore is discharged onto drag conveyors for transport to quench tanks. The leach liquor is concentrated to 50–60 g/L V_2O_5 and pumped to precipitation tanks. After several displacement washes, the leached calcine is removed from the leaching vats and discarded into the tailings dump.

The concentrated pregnant solution is initially precipitated as ammonium metavanadate (AMV). Excess ammonium chloride is added as a precipitating agent to the continuous flow of pregnant solution inside an air-agitated reactor. The slurry is then thickened and pumped into filter boxes. The thickener overflow, containing barren solution, is pumped to coal-fired flash evaporators where the ammonium chloride solution is concentrated and returned to the precipitation plant for reuse.

After filtration and washing, the AMV precipitates are discharged from the filter boxes and fed to externally heated tube spiral conveyor-type deammoniators. The vanadium pentoxide powder is then melted in furnaces heated with glow bars at around 850°C for the production of vanadium pentoxide flakes.

The production of AMV was stopped in 1974 and replaced with the ammonium polyvanadate (APV) precipitation route. Sulfuric acid is used for pH adjustment. The pregnant solution is initially adjusted to pH 5.5 before the required quantity of ammonium sulfate is added. The solution is then adjusted to pH 2 with further additions of sulfuric acid to promote APV precipitation.

The coarse bright-orange APV precipitate is pumped into filters for washing and dewatering. Deammoniation and fusion follow thereafter and are carried out using the same reactor setup as in the AMV route. Reactors were later replaced with a rotary dryer to improve efficiency. The fused vanadium pentoxide assays at 99.5% V_2O_5, 3.5% V_2O_4, 0.25% Na_2O, 0.15% Fe, 0.006% S, and 0.002% P.

The filtrate, containing the barren solution from the APV plant, is evaporated in a two-stage vacuum evaporator. The condensate is sent to the leach dams. The sodium sulfate salt, produced after flash drying, is fed back to the roasting kilns for reuse as sodium flux.

Evraz Highveld Steel and Vanadium. In 1960, Anglo American Corporation of South Africa established Highveld Development Company. The purpose was to study the viability of producing pig iron and vanadium-bearing slag from titaniferous magnetite ore and to conduct a market survey of these new products. The study demonstrated that the Bushveld Complex ore could be melted in a submerged arc furnace using the addition of carbon to selectively separate vanadium and iron from titania. The vanadium and iron were recovered as liquid pig iron with most of the titania being absorbed in the slag. The liquid pig iron was subsequently processed in a side-blown air converter to produce vanadium-bearing slag and pig iron.

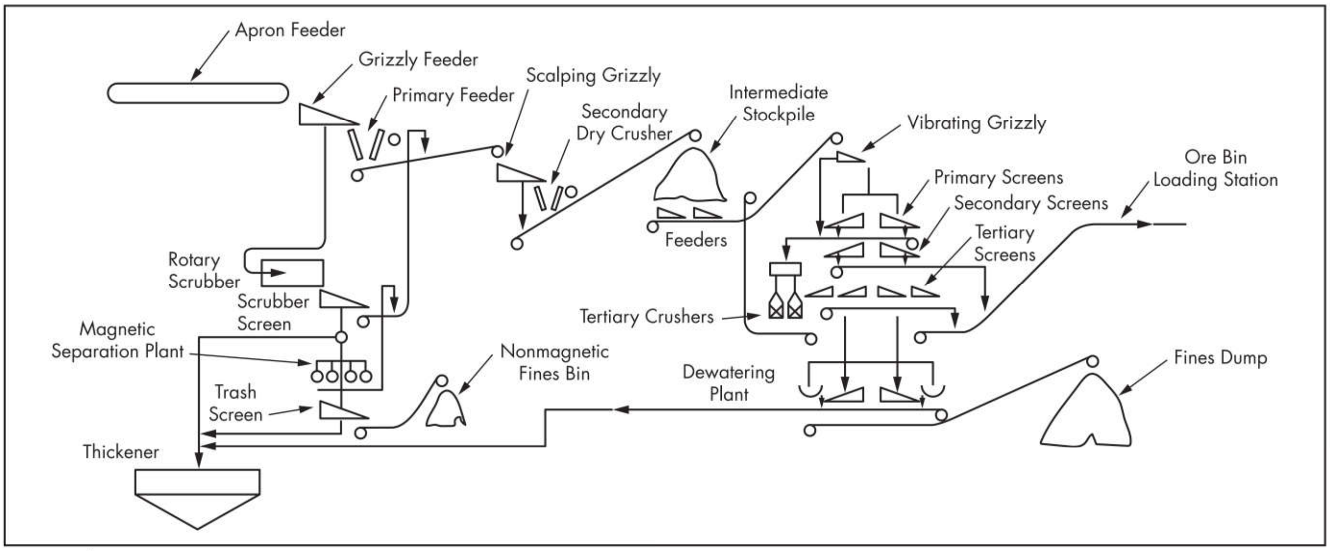
The Highveld process was developed to process ore from the Mapochs mine, which produces lump and fines iron ore. The ore treatment plant at the Mapochs mine is illustrated in Figure 3. Lump iron ore is processed through the Highveld steelmaking plant at Witbank (the city has since been renamed Emalahleni), and fine ore is sold to Vanchem Vanadium Products.

In 1965, Highveld Development Company changed its name to Highveld Steel and Vanadium Corporation (Highveld). By 1966, Highveld emerged as the global leader in vanadium production. In 2007, Evraz acquired an 85.1% stake of Highveld and then changed its name to Evraz Highveld Steel and Vanadium (Evraz Highveld) in 2010.

The Evraz Highveld processing plant comprises an iron production and steel facility with casters, a vanadium slag-crushing plant, a structural products rolling complex, and a flat products rolling complex. The iron plant treats the titaniferous magnetite ore in a pre-reduction process in 13 rotary kilns. Once reduced, liquid pig iron is produced in four open slag bath furnaces and two submerged arc furnaces with a combined annual capacity of 1,000,000 t of liquid pig iron (Evraz 2014). Vanadium slag is extracted at four shaking ladle emplacements in the steel plant, and the remaining liquid iron is processed into liquid steel in three basic oxygen furnaces and two ladle furnaces. The liquid steel is then cast into blooms and slabs for hot rolling, and the resulting billets are sold as semifinished product. In 2014, Evraz Highveld produced 7,130 t of contained vanadium in slag (Evraz 2015). The Evraz Highveld process flow sheet is shown in Figure 4.

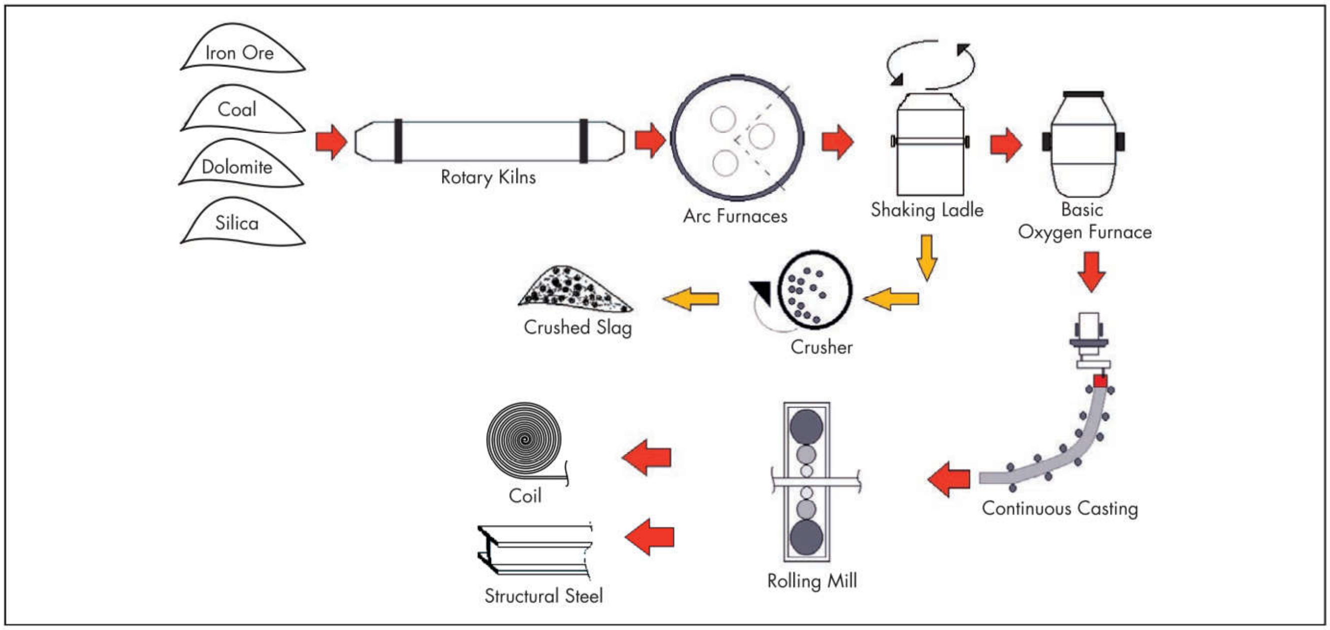
The 13 refractory-lined rotary kilns in the iron ore plant are each 60 m long (Rohrmann 1985; Steinberg et al. 2011). The rotary kilns are co-currently fired using pulverized coal. Combustion air is introduced into each rotary kiln at the feed end. This design prevents the particles from fusing together by allowing the charge to absorb heat. The temperature profile in the rotary kiln is regulated via the supply of air and pulverized coal and is maintained close to a maximum temperature of 1,140°C.

The titaniferous magnetite ore is pre-reduced to 50%–70% metallic iron. The pre-reduction step provides hot charge, thereby reducing power consumption in the arc furnace. Dolomite and quartz are added to flux the titania into slag. The hot kiln discharge is collected into hoppers from which it is transferred to skip bins before feeding into a submerged arc furnace.



Source: Rohrmann 1985

Figure 3 Ore treatment plant at Mapochs mine



Source: Steinberg et al. 2011

Figure 4 Evraz Highveld process flow sheet

In the electric submerged arc furnace, liquid pig iron, titania slag, and carbon monoxide (CO) gas are produced. The submerged arc Elkem furnaces used are of closed-top design. The shell, with a diameter of 14 m, is equipped with three 1.6-m-diameter Soderberg electrodes. The temperature is maintained at ~1,350°C.

Each furnace is equipped with two tapholes, which are alternately used. A weir placed in the tapping launder separates the liquid pig iron and slag. The hot metal flows into railroad transfer ladles, and the slag is collected into slag pots. The titania slag is then crushed. Any entrained metal particles are magnetically removed and recycled through the process.

From the arc furnaces, the pig iron is transferred to the steel plant. The steel plant consists of four shaking ladles, three 70-t basic oxygen furnaces, two ladle furnaces, and four continuous casting machines. The steel plant can produce slab, blooms, or billets at a production rate of 2,600 t/d.

Vanadium is transferred from the liquid pig iron to slag using a shaking ladle process. The shaking ladle follows soft oxygen blowing. The oxygen blows into a ladle to form iron oxide (FeO) and then reacts with vanadium to form slag enriched with vanadium oxide. The reactions of this mechanism are as follows:

$$2V + 3/2O_2 = V_2O_3 \text{ (in slag)} \quad \textbf{(EQ 9)}$$

$$Fe + ½O_2 = FeO \text{ (in slag)} \quad \textbf{(EQ 10)}$$

$$2V + 3FeO = 3Fe + V_2O_3 \text{ (in slag)} \quad \textbf{(EQ 11)}$$

Scrap and iron ore are used as a coolant. The bath temperature is controlled to below 1,400°C such that a high rate of vanadium oxidation and a low rate of carbon oxidation can be achieved. The addition of iron ore improves the FeO activity in the slag, which in turn enhances the oxidation of vanadium from the metal.

During blowing, most of the carbon is oxidized to CO or carbon dioxide (CO_2). Anthracite is used to replenish carbon. The blowing rate and anthracite addition need to be carefully controlled to prevent the anthracite from reducing the vanadium oxide back to metal. The metal is poured into a basic oxygen furnace. The slag is retained and transferred to the crushing and packaging plant. The vanadium slag typically contains 12%–24% V_2O_5. It is used as feedstock for vanadium oxide and ferrovanadium production.

Vanadium slag is crushed, milled, and packaged at the vanadium slag-crushing plant. It is then sold to Hochvanadium Handels (a wholly owned subsidiary of Evraz Highveld), which supplies it to Treibacher Industrie. In turn, Treibacher Industrie processes it further into vanadium products, predominantly ferrovanadium, for sale in the European market.

Vametco. Vanadium slag is also supplied to Bushveld Vametco Alloys, situated near Brits in the North West Province of South Africa, for toll conversion into products such as modified vanadium oxide and Nitrovan. These products are sold on global markets through East Metals. Vametco's primary production is from magnetite ore from its mine located near the processing plant. Vametco has an annual production capacity of 3,600 t of contained vanadium as Nitrovan.

Vanchem Vanadium Products. A small amount of the vanadium-enriched slag is also sold to Vanchem Vanadium Products (VVP), a subsidiary of Duferco of Switzerland. VVP also purchased fines iron ore from the Evraz Highveld Mapochs mine. VVP owns and operates a processing plant at Witbank, located ~10 km from the Evraz Highveld's steelmaking plant. The processing plant at Witbank can produce ferrovanadium, vanadium chemicals, and fused V_2O_5 flakes. The rated production capacity is approximately 5,400 t/yr of contained vanadium. The estimated production in 2014 was 4,000 t/yr of contained vanadium (TZMI 2015). VVP also holds mineral rights for vanadium-containing iron ore reserves in the Steelpoort area through Rakhoma Mining Resources. In addition, VVP owns and manages 50% of South Africa Japan Vanadium (SAJV), a joint venture between VVP and Nippon Denko Company, which produces ferrovanadium for the Japanese market.

Glencore Rhovan. The Glencore Rhovan operation is another major vanadium producer in South Africa, located near Brits in the North West Province. Glencore acquired the Xstrata Rhovan operation when Glencore and Xstrata merged as corporate entities. The Ba-Mogopa mine, in operation since 1989, supplies titaniferous magnetite ore to the Rhovan operation.

Vanadium is extracted from the magnetite ore via primary production. The ore is crushed, milled, and then upgraded by magnetic separation to produce a concentrate, which is then processed using a salt roast–water leach route. A mixture of concentrate and sodium flux is processed in a coal-fired rotary kiln. The leaching is performed in leach dams to recover the vanadium-bearing solution. Silica in the pregnant solution is removed via precipitation with aluminum sulfate and filtration. The purified pregnant solution, recovered from the filtration, is reacted with ammonium sulfate to form AMV. The AMV is filtered, dried and deammoniated, and fused into V_2O_5 flakes. A portion of the AMV is also converted in reactors to produce V_2O_3 or V_2O_5 powder.

The processing plant can produce the equivalent of 10,000 t/yr V_2O_5. Glencore Rhovan also has a conversion capacity to produce 7,800 t/yr FeV. In 2014, Glencore Rhovan produced a total of 9,435 t V_2O_5 (Glencore 2015). Figure 5 shows the Glencore Rhovan process flow sheet.

New Zealand

In New Zealand, vanadium is extracted as a by-product from the steelmaking industry (Robson 1973; Hitching and Kelly 1982). The steelmaking plant, located at Glenbrook, ~40 km southwest of Auckland, employs similar technology to that used in South Africa by Evraz Highveld.

New Zealand Steel produces ~15,000 t/yr vanadium slag with 15% V_2O_5 concentration, which is sold to Chinese convertors, to be processed into V_2O_5 and FeV. New Zealand Steel also exports ~750,000 t/yr of its iron sands concentrates to Tianjin in northern China as feedstock for steel and vanadium slag production at Chengde.

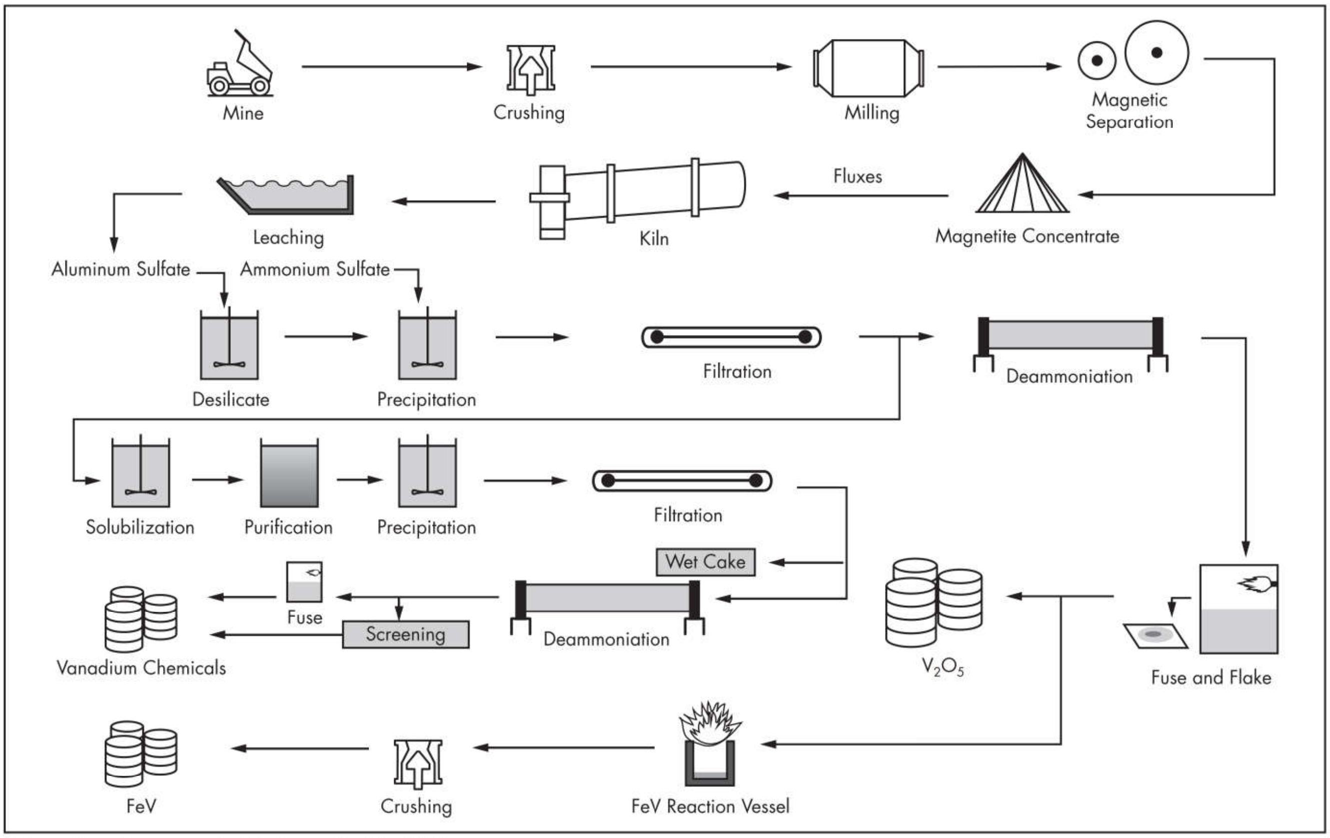
China

As discussed previously, blast furnace operation is unsuited for treating titaniferous magnetite ore. Nonetheless, a blast furnace operation using titaniferous magnetite concentrate has been successfully implemented in China (Zhou 2000; Taylor et al. 2006; Vermeulen 2009). It has been reported that the concentrate is mixed with high-quality iron ore sourced to dilute the TiO_2. This reduces the risk of reducing the high-melting-temperature titanium carbides and titanium nitrides into the hot metal. The vanadium-bearing concentrate is first reduced to hot metal in a blast furnace, and then the vanadium is oxidized into a slag phase by blowing oxygen into the hot metal in the converter. Taylor et al. (2006) reported that Panzhihua controls the slag basicity (the ratio of calcium oxide [CaO] and SiO_2) to suppress the reduction of TiO_2. Du (1989) observed that the silicon-to-titanium ratio should be lowered to <0.8 in the blast furnace to suppress reduction of TiO_2.

The titaniferous magnetite resources are located in Ma'anshan in Anhui Province, Chengde in Hebei Province, and Panzhihua in Sichuan Province. Panzhihua New Steel and Vanadium Company, a subsidiary of Panzhihua Iron and Steel Group Company (Pangang), is the largest vanadium slag producer in China. Chengde Xinxin Vanadium and Titanium Company is the second largest vanadium slag producer in China. Together, they constitute approximately two-thirds of the total vanadium supply in China (TZMI 2015). Table 1 shows the production capacity of the various vanadium producers in China (TZMI 2015; Panzhihua 2013).

Slag in China typically contains 14%–22% V_2O_5. The slag is then roasted with sodium or calcium salts. China produces ferrovanadium containing 50% and 80% vanadium. Apart from that, the vanadium extracted from the slag is also processed into V_2O_5 flake, V_2O_5 powder, vanadium nitride, and vanadium carbonitride.

Qin et al. (2015) reported that Pangang invested 290 million yuan and constructed a pilot plant in 2009 to investigate the feasibility of rotary hearth furnace direct reduction and electric arc furnace for extracting vanadium from titaniferous magnetite ore. The pilot plant has a production capacity of 52,000 t of pig iron with low carbon content, 5,900 t of vanadium slag, and 24,000 t of titanium slag.



Adapted from Xstrata, as cited in Ocean Equities 2011

Figure 5 Glencore Rhovan process flow sheet

The titaniferous magnetite concentrate is first pelletized and then charged into the rotary hearth furnace. The pellets are reduced to 85% metallics, then transferred into an electric arc furnace for deep reduction. In the furnace, the titanium slag is separated from vanadium-bearing hot metal. The titanium slag contains about 45% TiO_2. After desulfurization, the vanadium-bearing hot metal is transferred to a vanadium recovery station. At the recovery station, oxygen is injected from the surface of hot metal with nitrogen being supplied at the bottom of the ladle. The vanadium in the slag is approximately 12% V_2O_5. Approximately 80% of the vanadium reports to slag. The vanadium in slag is then recovered using salt roasting. With the titanium slag, a sulfuric acid process is applied to produce a titanium dioxide product. Titanium recovery of 80% is achieved.

Table 1 Estimated vanadium slag production capacity in China

Company	Region	Product	Capacity, t/yr V_2O_5
Panzhihua New Steel and Vanadium	Sichuan	Vanadium slag	47,000
Chengde Xinxin Vanadium and Titanium	Hebei	Vanadium slag	20,000
Jianlong Steel Industrial	Heilongjiang	Vanadium slag	10,000
Kunming Iron and Steel	Yunnan	Vanadium slag	2,000
Chuanwei Steel Group	Sichuan	Vanadium slag	10,000
Other		Imported, vanadium slag	8,000

Source: Panzhihua 2013

Russia

Kachkanarsky mining and dressing complex (KGOK), a subsidiary of the Evraz Group, mines titaniferous magnetite ore from an open pit at Kachkanarskoye in western Russia. The beneficiation plant consists of dry magnetic separation, two-stage milling, and three-stage wet magnetic separation, followed by dehydration (Evraz 2010; Moskalyk and Alfantazi 2003; Taylor et al. 2006).

It produces a concentrate assaying at 0.57%–0.66% V_2O_5. The KGOK facility can produce 10.9 Mt/yr concentrate, which is further processed to 4.0 Mt/yr sinter and 6.9 Mt/yr pellet. KGOK supplies 70% of its production to Evraz Nizhny Tagil Iron and Steel Works (NTMK). The remaining is supplied to Chusovoy Metallurgical Works (CMW), Magnitogorsk Iron and Steel Works, and Novokuznetsk Iron and Steel Works.

NTMK processes material from KGOK into vanadium-bearing slag and microalloyed steels using two-stage basic oxygen converters. The first stage involves the production of vanadium slag (16%–28% V_2O_5) and a carbon-bearing intermediate product (3% C, 0.03% V). In the second stage, the intermediate product is processed into various grades of steel. The process recovers ~80% of vanadium into slag.

Most of the vanadium slag from NTMK is sold to Evraz Vanady-Tula. Vanady-Tula, established in the 1970s, joined the Evraz Group in 2009. Vanady-Tula employs calcium roasting technology followed by hot acid leach to produce vanadium red cake, which is fused to V_2O_5 flake. Vanady-Tula converts a portion of its V_2O_5 production into 50% FeV and 80% FeV to sell in the Russian and Commonwealth of Independent States markets. It has the capacity to produce 7,500 t of contained vanadium as V_2O_5 and 5,000 t of contained vanadium as FeV. In 2014, it produced 7,309 t V of V_2O_5, of which, 2,755 t was converted into FeV at Vanady-Tula, 3,538 t was consumed by Evraz Nikom, and the remaining V_2O_5 was sold to third parties (Evraz 2015).

NTMK also supplies CMW with vanadium slag. CMW employs a silica-thermic process to produce ferrovanadium. The mixture of vanadium slag, V_2O_5, lime, and fluoride is fused and then reduced with silicon and aluminum powder. The first stage produces metal assaying at 35%–40% V and 9%–12% Si. The metal is refined in the second stage by successive additions of V_2O_5 and lime until the residual silicon content is less than 2%.

Australia

The development of the Windimurra project led to the first commercial production of vanadium in Australia. The Windimurra vanadium deposit was discovered in 1961, but construction of the processing plant only began in 1998. Precious Metals Australia (PMA) formed a joint venture with Xstrata Alloys (now Glencore) in 1998 to develop the Windimurra project, and Xstrata Alloys acquired 51% interest in the project. Mining commenced in December 1999 with the first shipment of vanadium taking place in February 2000.

The project comprised an open cut mine followed by a processing plant employing primary crushing, single-stage semiautogenous milling, and magnetic separation. The concentrate was subjected to grinding in a Vertimill before a final polishing step with magnetic separation to produce a concentrate for the downstream refinery processing plant. The vanadium in concentrate was extracted via salt roast–water leach route using sodium oxalate. The sodium oxalate was a by-product of Alcoa's alumina refining operations at Wagerup and Kwinana and therefore offered an advantage regarding reagent cost. The pregnant solution was subjected to desilication before precipitation. It was then subjected to deammoniation, fusing, and flaking for the production of vanadium pentoxide flakes with purity of 98%.

In June 2000, after six months in production, the mine produced 2,722 t V_2O_5; in 2001 it produced 4,763 t/yr V_2O_5; and in 2002, it produced 5,443 t/yr. The mine reached its operating target in August 2001, producing 7,257 t/yr V_2O_5 before the production level was reduced (Economics and Industry Standing Committee 2004). The processing plant processed predominantly weathered ore. Milling the soft weathered ore created excessive fines and therefore hindered magnetic recovery.

In February 2003, the mine was placed on care and maintenance with its permanent closure announced in May 2004. The decision to suspend production was caused by a prolonged period of low vanadium prices. The processing plant was partially dismantled with significant components sold and removed from the site.

In 2005, PMA regained 100% ownership of the Windimurra project and formed a subsidiary company—Windimurra Vanadium Australia (WVA)—to develop the project. PMA adopted a new process flow sheet involving three-stage crushing followed by high-pressure grinding rolls. The crushed ore was then upgraded by rougher-scavenger magnetic separation. The concentrate was reground in a ball mill before final polishing with cleaner-scavenger magnetic separation. The vanadium processing facility was similar to the historical operation by Xstrata-PMA. The new plant also incorporated a new ferrovanadium production facility. Sodium carbonate was used to replace sodium oxalate.

In 2009, PMA was unable to raise sufficient funds to complete the project, and hence WVA was placed in receivership. In 2010, Atlantic acquired the Windimurra project and completed the construction of the remaining processing facility. At the time of the purchase, the construction of the concentrator plant had almost been completed. Atlantic formed a subsidiary company, Midwest Vanadium Pty Ltd. (MVPL), to operate the Windimurra project. Atlantic completed the construction in 2011. Mining commenced in January 2012 with the first shipment of ferrovanadium reported in June 2012. The concentrator processing plant was unable to reach its nameplate capacity, mainly because of the incorrect selection and/or sizing of equipment in the crushing, milling, and beneficiation area.

Production ceased in February 2014 because of a hot work accident that caused a fire in the beneficiation facility.

Brazil

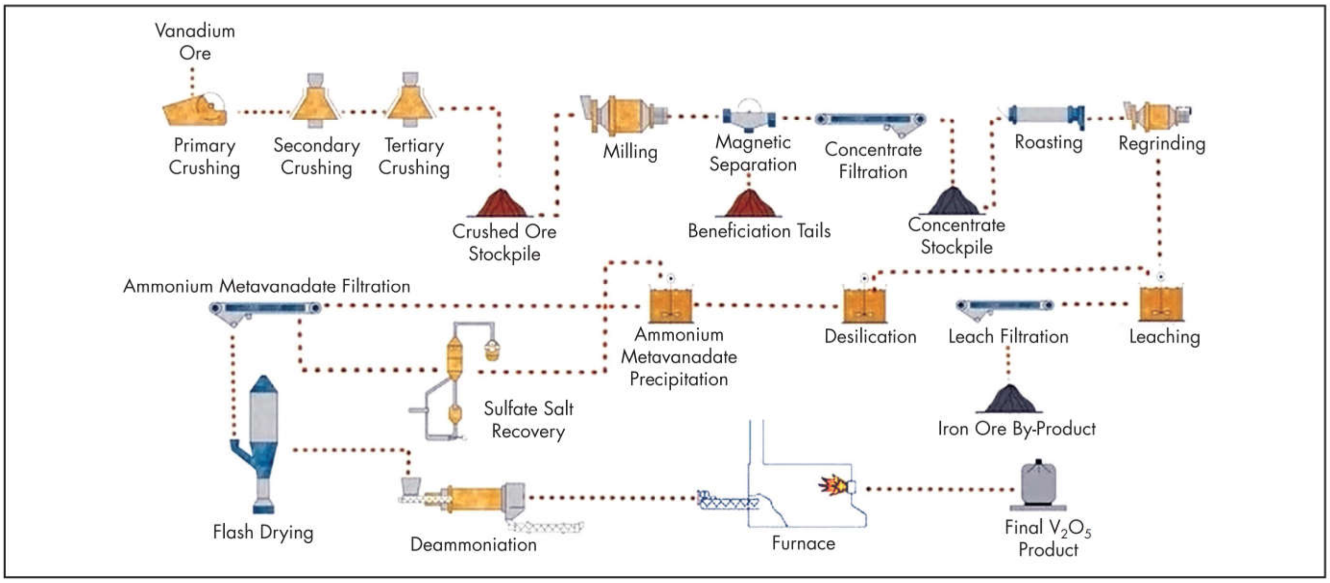
Largo Resources (Largo) emerged in Brazil as a new vanadium producer following the construction of the Maracas Menchen mine in 2012. This mine is located ~250 km southwest of Salvador (Arsenault et al. 2013). The mine phase I nameplate annual production capacity is 9,600 t of V_2O_5. Ramp-up to full production was achieved 2017.

The processing facility comprises three-stage crushing with an intermediate stockpile to provide continuous feed to a ball mill. The crushed ore is then milled in the ball mill before it is upgraded by magnetic separation. The concentrate is roasted in a rotary kiln using sodium carbonate and sodium sulfate. The hot calcine is conveyed to a regrind mill where the lump is broken down. Leaching is conducted in agitated tanks. The slurry is filtered using a vacuum belt filter. The pregnant solution is pumped to desilication tanks, where it reacts with aluminum sulfate for silica removal. Sulfuric acid is added to control the solution pH. The slurry is then filtered to separate the solid enriched with silica. The purified pregnant liquor is precipitated as AMV using ammonium sulfate. The precipitate is filtered and fed to a flash dryer and deammoniator to produce V_2O_5. The V_2O_5 is then melted and cast into flakes for sale. The barren solution is treated in evaporators to recover sodium sulfate salt for reuse in the rotary kiln. Figure 6 shows the process flow sheet of the Maracas mine.

OUTLOOK AND MARKET

The near-term outlook for vanadium production is for a very tight market to continue, as many vanadium producers have stopped production or gone out of business. In April 2015, Evraz Highveld went into business rescue (Marsden and Terblanche 2015), and much of the iron plant has been dismantled. The future of the steelmaking plant at Witbank and the Mapochs mine remains unknown. With suspended production at Mapochs mine, VVP was forced to stop production because of lack in supply of vanadium raw material.

In February 2015, MVPL was placed into receivership. The Windimurra mine and mill has not operated since February 2014, and the future of the project remains uncertain. Longer



Source: Arsenault et al. 2013

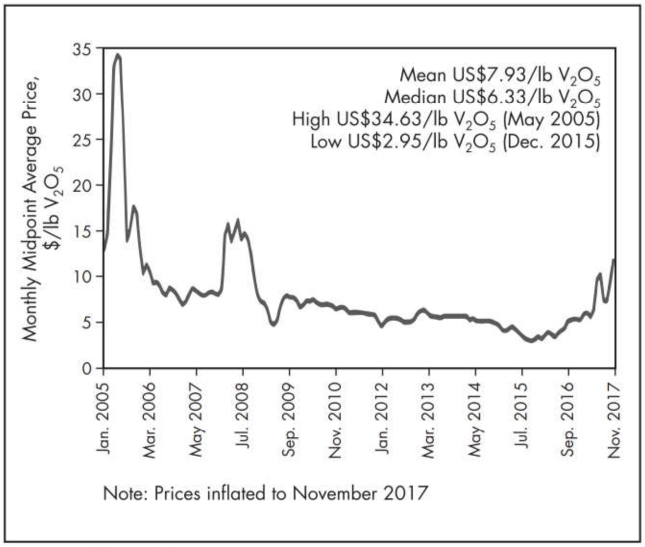
Figure 6 Maracas process flow sheet

term, vanadium demand is projected to grow at its historic compound annual growth rate of 6.6% (Perles 2015; TZMI 2015). Growth in global steel production and the increase in specific vanadium consumption rates within the steel industry continue to drive vanadium growth. Vanadium intensity of use in North America is almost double that in China today. As China increases the percentage of alloyed steel production, the growth in demand for vanadium is expected to exceed that of growth in steel production. Growth in vanadium demand has exceeded vanadium production capacity, and all excess inventory has been worked out of the system. Additional new production is required to be brought on line.

Numerous vanadium projects around the world can be brought into production over time. Many of these are based on titaniferous magnetite ore bodies that require significant capital investment to be brought online. The projected cost to bring a greenfield mine and mill into production is US$300–$500 million, with an anticipated project timeline of four years.

Today, vanadium is used not only as an alloying component in steel and titanium alloys, but also as a catalyst for chemical reactions (Perles 2010, 2012). In 2014, world vanadium production amounted to 89,000 t of contained vanadium (Vanitec 2014). Approximately 91% of vanadium is consumed in the steelmaking industry (Roskill 2015). An alloy called *ferrovanadium* is used to produce higher strength steels for use in the construction and automotive and transportation industries and in manufacturing high-speed tools. The application of vanadium in the production of titanium alloys for aerospace and industrial purposes represents 4.5% of global demand. Approximately 3.5% of vanadium consumed in 2014 was used in petrochemical, catalyst, and pollution-control applications and in production of consumer products, such as ceramic pigment, special glasses, and so forth. The remaining 1% was used in energy storage applications.

As the world turns more and more to green energy power production, utilizing solar and wind power generation, there is much discussion about vanadium storage batteries and the significant potential demand from this area. Substantial investment has been made in this area as a result of improvements in cell technology and electrolyte chemistry. Large megawatt batteries are now being produced and placed into service. With continued growth, this application is expected to be a major consumer of vanadium in the future.



Note: Prices inflated to November 2017

Courtesy of Terry Perles

Figure 7 V_2O_5 monthly midpoint average price

The vanadium price is reported by the London Metal Bulletin (LMB) for European and Asian market pricing and by Ryan's Notes for North American pricing. V_2O_5 is typically priced per pound V_2O_5 contained, and FeV is quoted per kilogram vanadium by LMB and per pound vanadium by Ryan's Notes. Pricing is driven by supply and demand and has been quite volatile through history, with large swings in pricing occurring based on the balance between supply and demand. V_2O_5 pricing as quoted by LMB from 2005 through January 2018 is shown in Figure 7.

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