Trends with Titaniferous Magnetite Processing for Vanadium Extraction

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KEYWORDS

Titaniferous magnetite, ilmenite, mineral liberation, QEMSCAN, project development, Reed Resources Ltd, Barrambie Vanadium project, HPGR, Windimurra, Windimurra Vanadium, Aurox Resources, Balla Balla, LIMS, rare earth magnets, Vertimill, silica removal, reverse flotation, SLON, WHIMS, sodium carbonate, sodium oxalate, pelletising, pre oxidation, roasting, desilication, sodium vanadate, ammonium vanadate, fusion, flake vanadium pentoxide, ferrovanadium.

ABSTRACT

Titaniferous magnetite deposits are a significant source of vanadium for use in high strength steel alloying and other chemical applications.

The mineralogy of the deposits varies markedly and the ore characteristics strongly influencing the process route selected and the metallurgical outcomes. Characterisation of the ores reveals the presence of magnetite, ilmenite and other minerals such as spinel hematite and goethite with variable degrees of weathering along with weathered products of host rock. The standard processing route is to crush, grind and magnetically recover a concentrate for salt roasting to produce a soluble vanadate.

Ore beneficiation is practiced to generate an iron based mineral concentrate containing much of the vanadium with low silica levels of 2%. Typical processing problems encountered are fine liberation size, over grinding of the magnetite and variable response to magnetic separation resulting from the weathering profile.

Beneficiation options are restricted, and generally focused on producing a combined iron and titanium rich concentrate containing vanadium due to the fact that ilmenite

and magnetite and their products of weathering are magnetic and have similar specific gravities making their separation difficult. The ilmenite usually contains low levels of vanadium making its separation highly desirable from the iron mineralisation containing higher levels of vanadium.

Salt roasting of vanadium ores followed by water leaching has been the standard processing route for many years. The cost of suitable sodium salts, availability of capital and increasing energy costs and energy availability are critical factors in determining the viability of aspiring vanadium producers. To date, only Windimurra has acquired full capital funding, secured energy and sodium salt supplies at suitable cost that enable the construction of the project. Low overall recoveries of vanadium to concentrate roasting at up to 1200^0 C are critical cost issues.

In this paper, factors influencing the recovery of vanadium are reviewed and emerging processing trends explored. The important features of the processing of titaniferous magnetites have been condensed from the literature, published works, company websites, our own work and personal communication.

TITANIFEROUS MAGNETITES

Titaniferous magnetites are widely distributed throughout Australia and overseas and represent the largest known reserves of vanadium amenable to metallurgical processing.

Because the ores are rich sources of iron the most common processing is via a blast furnace to produce vanadium and titanium rich slags which are subsequently processed to produce vanadium pentoxide and titanium slags for the sulfate process. (LD slag produced by SSAB, Highveld process, NZ Steel process, Pan Steel process, Russian NTMK process, etc),

Production of vanadium is dominated by South Africa, Russia and China. With the advent of Windimurra commencing production in 2008, and the possible development of Barrambie and Balla Balla, Australia will once again be a significant vanadium product producer. *NB Whilst Balla Balla will be an iron ore producer by its own admission, its concentrate does contain vanadium.*

The titanium is generally present as ilmenite; $FeTiO_3$ which is believed to contain relatively low levels of vanadium compared to the iron based minerals. Vanadium exists in the magnetite spinel substituted for ferric iron i.e. $FeO.V_2O_3$ replaces $FeO.Fe_2O_3$.

Attempts to separate ilmenite from the magnetite have thus far proven difficult although flotation and gradient magnetic separation show promise. In some cases the liberation size of a portion of the titanium minerals is less than 5 microns with fine lathes of titanium mineralisation running through the iron mineralisation.

All titaniferous magnetite deposits exhibit the classic oxidation profile down to the water table this results in changing mineralogy and alteration of the mineral responses to metallurgical processing as the deposit changes from unweathered primary ore to highly weathered oxidised ore. The ores of the Western Australia vanadium belt have many parallel mineralised ore lenses of varying thickness separated by zones of weathered rock. Within these broad classifications vanadium can both be incorporated into these interlens weathered rock zones and enriched in portions of the ore lens in mineralisation that does not easily respond to traditionally applied mineral processing practices. This has led to some references being made to “good” and “bad” vanadium within an ore body based on the ease of recovering it to the concentrate.

On the macro scale, the oxide ores are typically soft, containing clays and result in low yield to concentrates, with associated losses of vanadium to tailings while vanadium upgrading of up to 40% can be achieved. The concentrates respond well to salt roasting with high extractions of vanadium from the calcine of 80 to 90%, but overall recovery of vanadium can be low, approximately 40 to 60%.

The primary ores are typically very hard and do not contain clays and can result in high yield to concentrates with vanadium upgrading of up to 20%. The concentrates response to salt roasting is more problematic (IS IT?) but with 80 to 90% extraction of vanadium from the calcine, the overall higher recoveries can be as high as 75%.

The process yields and vanadium recoveries have to be accounted for in the process plant design and in determining JORC compliant ore reserves. This is not a simple task given the high degree of variability exhibited by some of the orebodies, particularly in the weathered zones.

The standard vanadium processing route involves magnetic concentration to produce a clean concentrate usually containing less than 2% silica. Regrinding of the concentrate can be used to meet the target silica grade by reverse flotation using amine collectors. Thereafter, vanadium is extracted by salt roasting, leaching, solution purification and finally vanadium precipitation. The saleable product is either Vanadium Pentoxide (V_2O_5) or Ferro Vanadium.

A number of alternative vanadium extraction methods such as acid leaching can be technically effective but are costly due to high acid consumption. Basic leaching does not extract any vanadium.

AUSTRALIAN PROJECT LOCATIONS

There are three major vanadium projects currently in Western Australia at varying stages of readiness for production.

Windimurra Mine is 600 kms north-east of Perth, near Mt Magnet (Figure 1) is under construction and will be commissioned for production of ferrovanadium in 2008. Windimurra is the most advanced new vanadium producer worldwide.

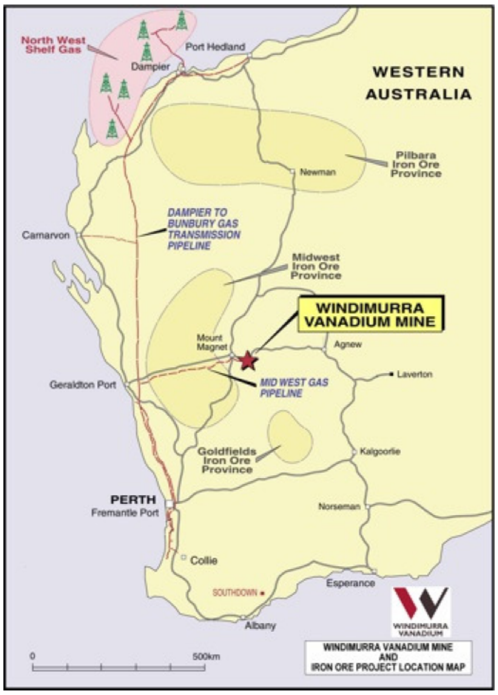

Figure 1 Windimurra Project

The Barrambie deposit is at feasibility study stage and is located alongside the Sandstone-Meekatharra Road, about 75 km north of Sandstone and 115 km south of Meekatharra (Figure 2), where the No.1 Rabbit Proof Fence crosses the road.

Figure 2 Barrambie Project

Balla Balla is located close to the north-west coastal highway midway between Roebourne and Pt Headland. (Figure 3) and is seeking statutory permits and capital for construction.

The start up project for Balla Balla if successful would result in the export of the vanadium values contained in a magnetite concentrate with no Australian based vanadium extraction processing plant.

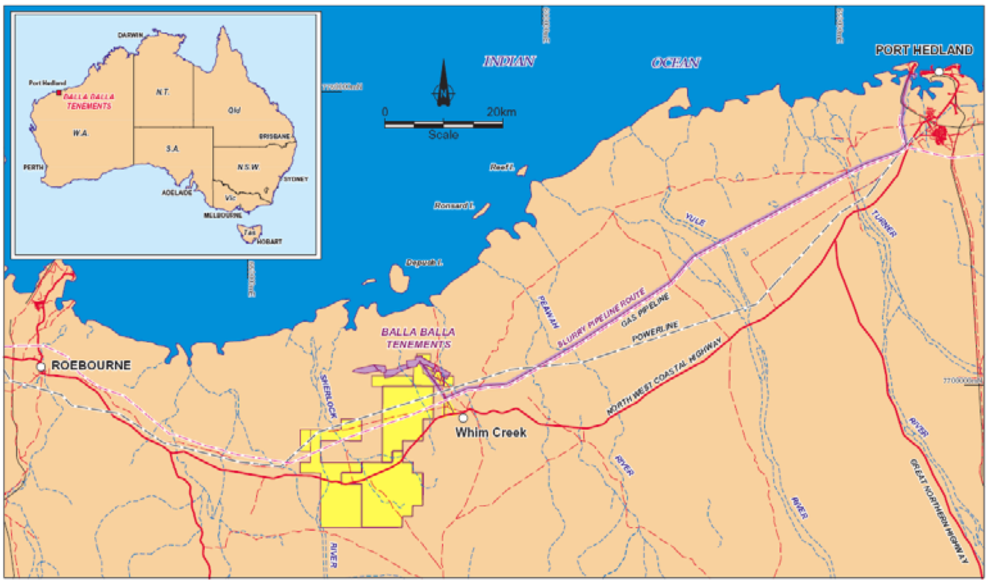

Figure 3 Balla Balla Project

COMMINUTION

The comminution circuit differences between Windimurra and the emerging Australian projects Balla Balla and Barrambie reflect the significant differences with the ores being processed.

The old Windimurra comminution circuit designed predominately for weathered ore was a single stage SAG mill and suffered from overgrinding of the high specific gravity magnetite. The new Windimurra project with a predominantly unweathered hard ore includes a High Pressure Grinding Rolls (HPGR) and coarse cobbing at 500 microns ahead of a regrind ball mill.

The Barambie project designed for weathered ore at 3.2 Mtpa on the other hand, includes a jaw crusher ahead of a scrubber (removes clays) and secondary crushing with a final ball mill grinding stage to P_{80} 75 microns.

The Balla Balla project with an all primary ore to treat 6Mtpa of feed includes primary crushing and a conventional SAG ball mill grinding circuit with a P_{80} grind size of 106 microns. (Figure 4)

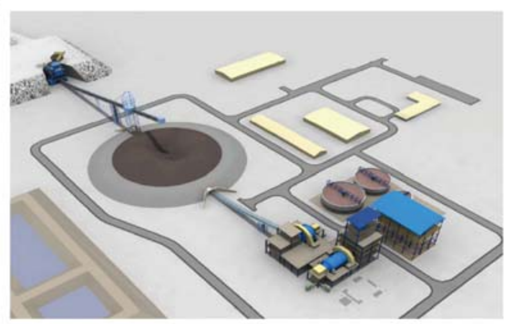

Figure 4 Balla Balla Comminution Circuit

BENEFICIATION

Beneficiation is a relatively low cost, low process risk part of the process and rarely the project bottleneck.

Though mineralogically slightly different, beneficiation processing for vanadium of the titanomagnetites has many similarities to the processing of magnetite and hematite based iron ores that require upgrading before marketing.

Magnetic separation is universally the accepted process route even though there may be a place for gravity, DMS or Jigs and the flotation processes. Desliming of the feed ahead of magnetic separation, at say 10 microns, has improved overall vanadium recovery and was used on the old Windimurra project and will be included at Barrambie.

The characteristic poor magnetic response of the weathered ore compared to the primary ore has significant implications for overall vanadium recovery and process costs. The implications flow through to the selection of equipment. Results from a beneficiation test program, (Table 1), which demonstrate the variation that can occur in the location within the plant circuit that the vanadium values report to, and values in grade of the concentrate produced.

		Test Sample Code	
		V12	V16
Head Grade	$\%V_2O_5$	0.81	0.84
Vanadium Recovery	Overall	65.0	69.0
Split Between			
	LIMS	0.2	45.9
	WHIMS	98.8	55.1
Product Grade	$\%V_2O_5$	1.34	1.12

Table 1 Variability in Magnetic Response

The Windimurra circuit consists of coarse magnetic separation followed by regrind and dry stacked tailings. Windimurra is targeting predominately unweathered ore with a declared weathered to unweathered ore ratio for the project of 20/80.

Barrambie has opted for Low Intensity Magnetic Separation (LIMS) and Wet High Intensity Separation (WHIMS) with a regrind ball mill. The WHIMS being necessary for the weathered nature of the orebody.

Balla Balla has magnetic separation and also has a majority of primary ore.

Over grinding of magnetite was a significant problem at Windimurra and all projects are endeavouring not to repeat these problems. The over grinding resulted in lower magnetic susceptibility utilising Rare Earth Drums (RED's).

The SLON magnetic separator developed and used in China on low grade hematite ores has been tested on titaniferous magnetites as an alternative to the WHIMS, but no obvious benefits are apparent.

Barrambie are considering utilising reverse flotation to meet the silica specification in the concentrate.

Both Barrambie and Balla Balla have not stated their intention regarding this aspect.

QUALITY CHARACTERISTICS

The concentrate quality is very important for suitability as roast feed. There has been a significant amount of work based on defining acceptable feed quality for all projects.

The general consensus is that an upper limit of 2.2% silica in the concentrate is acceptable. Above this level salt consumption is increased and vanadium recovery during leach extraction is reduced quite dramatically.

QEMSCAN has proven very beneficial in determining locking/liberation and the nature and occurrence of the minerals present, (Figure 5).

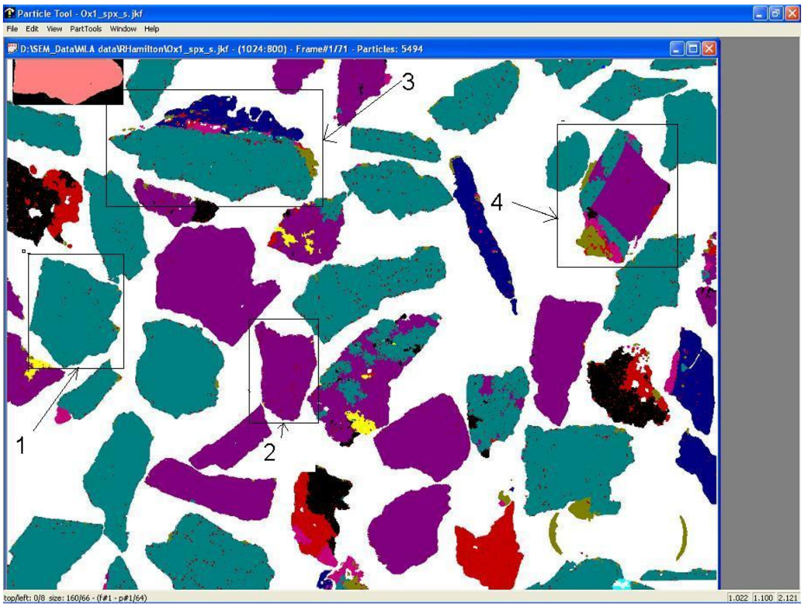

Figure 5 QEMSCAN on Barrambie Ore

1. 100% liberated ilmenite
2. 100% liberated titanomagnetite
3. A large particle of ilmenite with other minerals adhering
4. Three small particles of ilmenite with other minerals partly surrounding a large grain of titanomagnetite.

ROASTING

Normally the vanadium is present in the concentrate in the trivalent state and to produce water soluble pentavalent vanadates, both oxidation and reaction with a sodium salt are necessary as represented for sodium chloride by Equation 1.

$$2NaCl + O_2 + H_2O + V_2O_3 \blacktriangleright 2NaVO_3 + 2HCl \qquad \text{Eq1}$$

More basic vanadates can be produced by Equation 2.

$$2NaCl + H_2O + 2NaVO_3 \blacktriangleright Na_4V_2O_7 + 2\ HCl \qquad \text{Eq 2}$$

The sodium vanadates produced are very water soluble and this is the intention of the roasting process.

Typical salt levels are 5% to 10% wt/wt and as the sodium component of the salt is the required reagent for the vanadium process, several salts have been used in operational practice. The most favoured salt in modern processing is sodium carbonate which has superseded the use of chloride, oxalate and sulphate salts. Although, the latter is produced and recycled as a component of reducing overall sodium loss.

The cost of transport and availability makes the purchase of by product oxalate from the alumina industry prohibitively expensive (the original Windamurra project ran with an oxalate solution satisfactorily) and Windimurra and Barrambie have elected to use sodium carbonate. Sodium chloride is the lowest cost but lower vanadium recovery and the high potential for corrosion problems make it less desirable.

Roasting is the high CAPEX and high risk part of the business. Energy and salt costs are major process costs as well as refractory service life. Reducing the mass and increasing the grade improves process economics. Ultimately the kiln will be the plant treatment rate limiting stage.

The new Windimurra will use their existing kiln and satellite cooler (Figure 6).

Barrambie will install a new kiln and the majority of the concentrate will be from ore that is weathered in nature.

Balla Balla will sell a concentrate grading 58% iron and 1% V_2O_5 and does not include any further on site processing.

The presence of silica or silicates in the roasting kiln feed will consume sodium and impair the water leach recoveries if above nominally 2.2% because of the generation of glassy silicates containing insoluble vanadium. The presence of silica levels above 2.2% see a corresponding rapid drop off in vanadium recovery.

As a measure to minimise silica levels in the kiln feed regrinding and magnetic cleaning of the concentrate was undertaken for the old Windimurra project using a METSO Vertimill. The Barrambie Projects are expected to follow this same practice.

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Adding alumina has been undertaken where silica is an issue as reported in the literature, but neither project is doing this.

Required roast temperatures tend to be higher for the titaniferous magnetites (1200^0 C) and lower for the magnetites (900°C). Natural gas is a much cleaner fuel and results in less contaminant in the final product.

Floating silica using amines in a reverse flotation practice has shown positive results for Barrambie. This technique is commonly used for magnetite iron ores in North America and in hematite ores in China.

Fineness of grind is important because the roasting reaction rate increases with surface area. However, too fine a feed will result in excessive concentrate being blown out of the roasting kiln. Too coarse a grind can result in low vanadium extraction rates in leaching.

Pelletising the feed has a number of benefits; allowing intimate contact of the sodium salt, reduced dust losses improved refractory life and higher extractions are achieved at lower temperatures. The production of high strength pellets is an art and generally a finer grind produces a higher strength pellet. Significant energy will be consumed to fire pellets to increase their strength. Though a practice in the early days of the salt process commercial operation, neither project is considering pelletising at this stage.

The salt process requires that the iron mineralisation is fully oxidised when in the roasting kiln to ensure that the vanadium-sodium reactions take place to their full extent. Separate pre oxidation of primary magnetites is not being considered by either project though kiln operations, if conducted with excess air, will ensure that oxidation takes place.

Figure 6 Windimurra Operating 2004

LEACHING & DESILICATION

The roasting kiln operates at the melting point of the sodium phases generated and so the calcine produced will be lumpy in nature. Despite this the sodium vanadates are readily soluble in water.

The old Windimurra project utilised static in ground batch leaching vats which were successful and the new Windimurra has retained this technology. Continuous calcine milling followed by agitated tank leaching is being considered for Barrambie to improve recovery.

Once extracted into water the vanadium is separated from associated dissolved silica through aluminium precipitation. This stage was originally operated as a batch process. It is thought that Barrambie are looking at making this stage continuous.

AMMONIUM METAVANADATE

With silica free solution the processing route progresses to precipitation of the vanadium as an ammonium metavanadate before thickening and filtration. This stage used to be a batch process but developments over recent years overseas have shown that a continuous process is achievable and it is expected that both Windimurra and Barrambie projects will follow this route.

VANADIUM PENTOXIDE

Vanadium Pentoxide flake was the product produced from the ammonium metavanadate through continuous calcining at the old Windimurra project. Its quality was excellent because of the clean nature of the ore and the use of gas in the kiln rather than coal as practised in South Africa.

Windimurra will produce Ferrovanadium. Barrambie is examining the production of Ferrovanadium as an improvement to the marketing of the product.

FERROVANADIUM

The addition of a Ferro Vanadium circuit either to convert vanadium pentoxide (V_2O_5) to ferrovanadium (FeV_{80}) or generate it directly through a vanadium trioxide route, V_2O_3 as the final product or as part of a mixed product stream is becoming more common. Usually this will add significant value to the project because the ferrovanadium product achieves a price premium over vanadium pentoxide.

FeV Alumothermic Reduction

$3V_2O_5 + 10Al + 6zFe$ ► $6(Fe_zV)$alloy $+ 5Al_2O_3$

Note: z is a variable between 1 and 7.

Electric Arc Furnaces (EAF) are commonly used and the reaction becomes autogenous at 950°C. The charge consists of flake vanadium pentoxide or vanadium trioxide, aluminium scrap, iron scrap and lime or fluorospar. The slag is poured off and typically vanadium recovery to FeV is 95%.

EMERGING TRENDS & CONCLUSIONS

Vanadium projects are currently undergoing resurgence. The price for vanadium pentoxide has recovered from the disastrous lows of 2003 which shut down projects such as Windimurra when the price dropped to US$0.90/lb. China's entry to the World Trade Group and the growth in the steel industry, more particularly for high tensile steel, have seen prices at historic highs.

The trends for "new vanadium projects" are diverse. The ores are highly variable and weathering leads to a reduced overall vanadium recovery. The concentrate grades for the Australian projects are typically 1.0 to 1.4% V_2O_5 whereas South African resources are typically 2% V_2O_5.

Energy costs are going to be a significant factor for all projects. The flowsheets and approach are very different for the three projects under development in Western Australia. Balla Balla has taken the simplest route and will sell concentrates on the basis of payment being 'Hamersley Fines". Windimurra will be an integrated ferrovanadium producer. Barrambie anticipates going through to mixed product flake vanadium and ferrovanadium.

HPGR is an emerging trend for new iron ore projects and Windimurra have specified HPGR as the preferred option. The energy savings are reported to be approximately 15%.

The preference is for magnetic separation and LIMS or WHIMS with a move away from a sole dependency on Rare Earth Drums (RED) as previously used at the old Windimurra project.

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The dry stacking of tailings to reduce water consumption is a novel approach to water conservation.

Reverse flotation has been used on magnetite concentrates in the iron ore industry for many years and this is a novel approach to a perennial problem with vanadium processing.

Even though pelletising is widespread in the iron ore industry it has not been taken up for the vanadium projects.

Sodium salt recovery combined with evaporation and waste heat utilisation to reduce sodium carbonate costs is an approach used in some vanadium plants to reducing what is a major cost for the Barrambie project, although those plants have experienced significant difficulties in meeting emissions limits as a result. Even though oxalate from the alumina industry was low cost and provided excellent recoveries during roasting the trend has been not to use it because sodium carbonate has a lower transport cost. Windimurra holds exclusive rights to the process that uses sodium oxalate to produce vanadium and no approaches have been made to Windimurra regarding permission to license the process.

Agitated tank leaching has been specified for Barrambie in addition to calcine grinding to enhance leach recovery.

Windimurra is an integrated Ferrovanadium producer. Mixed pentoxide and Ferrovanadium product is the preferred option for Barrambie. The value added premium for FeV being the driver for what is a simple process step.

Balla Balla are undertaking a study to recover ilmenite from their tailings. Barrambie have no current plans to do this.

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