AUSTRALIA'S DOMINANCE IN THE TITANIFEROUS FEEDSTOCKS MARKET

THE COOLJARLOO PROJECT

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SYNOPSIS

Australia is the largest supplier in the world of titaniferous feedstocks, exporting the majority of ilmenite, rutile and synthetic rutile production to Europe, the United States of America and Asia.

This paper describes the forces which drive the market for titaniferous material, the titanium dioxide pigment production processes, the changes in future pigment manufacturing methods and the shift this will cause in the feedstocks markets.

The importance of the production of titanium tetrachloride as an intermediate feedstock for pigment and titanium metal production is discussed.

Minproc Holding Limited and Kerr-McGee Chemical Corporation are developing the world's first fully integrated "mine to pigment" project in Western Australia. The Cooljarloo project has more than 24 years supply of titaniferrous minerals available for processing into pigment, synthetic rutile titanium metal and other associated products.

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1.0 INTRODUCTION

The mineral sands industry worldwide is relatively young. Demand for titaniferous raw materials increased rapidly with the outbreak of World War II and the inception of most pigment and titanium metal production can be traced back to this world event. The cessation cf hostility allowed the mineral sands business to develop, having emerged during the war from its embryonic 1930's form to the current general structure.

Australia's mineral sands industry, which had been intermittent in operation from its early years in the 1870's, matured during World War II and in 1944, the Commonwealth of Australia placed a strategic ban on the export of mineral sands concentrates. The market weakened in post war years, recovered in 1950 and has expanded since that time. Australia is the major producer of mineral sands in the western world and accounts for more than 60% of titaniferous minerals in the world today.

This paper will not discuss non-titaniferous material but the associated zircon which is generally recovered with Australian mineral sands concentrates is an important product, as is monazite, for rare earth extraction.

The Cooljarloo project is the sole vertically integrated "mining to pigment project" anywhere in the western world.

Some details of the Cooljarloo project will be discussed in conclusion of this paper to illustrate a fully integrated mining, beneficiating, upgrading and processing venture in titaniferous materials.

Figure 1 depicts the industry structure and shows the varying stages of processing of titaniferous materials and the end uses of these products.

Ilmenite production forms the basin of the majority of titaniferous feedstocks that are consumed by synthetic rutile plants of direct-feed, sulphate pigment plants. Synthetic rutile, natural rutile and a higher grade slag are used for chloride process pigment production.

Hard rock mined ilmenite is treated via a slagging process which produces a generally lower grade titanium dioxide product.

It is significant to titanium metal production to recognize the output of titanium tetrachloride as an intermediate step in the production of high purity titanium dioxide pigment. Titanium tetrachloride is the primary feed for the manufacture of titanium metal by the Kroll, Hunter or Ginatta processes.

MINING



Figure 1. Mineral Sand Processing Flow Sheet

2.0 THE HEAVY MINERAL COMMODITIES

Heavy minerals are mined and beneficiated, mostly from unconsolidated beach and dune sand, but also from hard rock deposits. The rutile, ilmenite and zircon products and by-product monazite and xenotime are processed to extract their metal oxides which are consumed in a multitude of end uses mainly associated with computors, communications and aerospace industries.

2.1 Market Model

Figure 1 illustrates the general titaniferous material flow which is driven by the following forces:

- * The demand for paint, paper and plastics essentially determines the demand for titanium dioxide pigment.
 93% of pigment is consumed in these markets.
- * Pigment demand determines the demand for titanium bearing minerals rutile and ilmenite (in its various forms).
 - 92% of titanium is consumed in the pigment form
 - 4% in the form of rutile and high titanium bearing mineral mixtures
 - 3% as titanium metal.
- * The demand for rutile and ilmenite determines the supply of zircon and rare earth oxide bearing monazite and xenotime.
- * The preference for different titanium bearing heavy minerals is in part dependent on their titanium dioxide content. Table 1 shows that natural rutile has the highest titanium dioxide content while primary ilmenite has the lowest. Between these two end members lies a range of products derived from ilmenite. Secondary ilmenite and leucoxene represent naturally upgraded derivatives of primary ilmenite while synthetic rutile and slag are manufactured from secondary ilmenite and primary ilmenite respectively.

	Table 1 Titanium Dioxide Bearing Minerals						
	Natural Rutile	Synthetic Rutile	Slag	Leucoxene	Secondary Ilmenite	Primary Ilmenite Sand Rock	
Titanium Dioxide Content	(%)95	92-95	75-86	65-98	58-62	50-58	35-46

5.5

2.2 Market Segments

This simplified market model markets for example, the quality and mix of heavy minerals are often as important as deposit grade in determining the economics of mining and hence mineral supply. Some heavy mineral producers further segment supply by upgrading the quality of their ilmenites to either slag or synthetic rutile (see Figure 1).

The demand for "upgraded ilmenites" and other titanium bearing heavy minerals, while generally governed by the demand for titanium dioxide pigment, is also determined by the type of pigment production process. For example, pigment production using the chloride process depends on the availability of high grade titaniferous bearing heavy minerals while the sulphate process uses lower grade feedstocks. In addition, a variant on the chloride process developed by Du Pont uses a blend of high and low grade titaniferous minerals.

The various market segments are identified in Figure 2 for the chloride and sulphate pigment production processes. Slag is now the most important raw material for plants using the sulphate process while synthetic rutile represents the most significant feedstock for chloride plants. Secondary ilmenite is also an important raw material for chloride plants, however its use is restricted to the Du Pont process.





2.3 Titaniferous Feedstocks For Sulphate Process Pigment Plants

While titanium dioxide content has a strong bearing on the choice of raw material there are several other equally important factors. In the case of pigment plants using the sulphate process, primary ilmenite is an ideal feed because of its relatively large surface area. However, slag now supplies 54% of this market and will increase its share for the following reasons.

- * Supplies of good quality primary ilmenite are declining.
- * Slag is the only suitable alternative to primary ilmenite as:
 - secondary ilmenite can not be processed due to its low surface area.
 - synthetic rutile can not be processed because it is insoluble in sulphuric acid.
- * Slag reduces solid waste production and increases the plant's titanium dioxide capacity. It therefore allows sulphate plant operators to:
 - comply with new environmental standards, particularly in Europe and Japan.
 - reduce unit operating costs.

While these arguments present an appealing case for increasing slag use, each plant has to balance these benefits against the much higher cost of slag, compared with primary ilmenite (see Figure 3).



Figure 3. Cost Per Titanium Dioxide Unit of Raw Materials

2.4 Titaniferous Feedstocks

Pigment plants using the chloride process are also adjusting their feedstock requirements to use a greater proportion of synthetic rutile. These adjustments are occurring for the reasons listed below.

- * The supply of natural rutile is static and pigment producers are faced with greater competition for this raw material from the welding rod market.
- * Synthetic rutile is cheaper than rutile and has a higher titanium content than slag (see Figure 3).
- * High grade slags (85%+ titanium dioxide) have not achieved a high market acceptance. This is largely because alkalis in the slag reduce the recovery of titanium dioxide and because additional capital expenditure is required before pigment plants can handle slag.
- * Slag producers are also experiencing some difficulty in expanding their production of high grade material. South Africa produces a large amount of undersized slag during the crushing process which is unsuitable for chloride process pigment production. Therefore it is faced with the difficult task of reducing the amount of undersized material if it is to increase capacity.

The chloride process plants, based on Du Pont technology, are also likely to use more synthetic rutile in the future. At the present time they are heavily dependent on secondary ilmenite which is increasingly being consumed in the production of synthetic rutile. There is also an ever present threat of tighter waste disposal standards in the United States which, if they eventuate, would force Du Pont to use higher grade feedstocks.

Pigment manufacturers experience problems with low titanium oxide feedstocks, as the iron must ultimately be rejected from the process and be disposed of in an environmentally acceptable manner. The Cooljarloo ilmenite has lower iron content and produces comparatively minimal waste in the upgrading process to synthetic rutile. All neutralized waste produced will be buried in the Cooljarloo mining pit and the areas will be progressively rehabilitated as mining and production proceed.

In the full integration of titaniferous materials processing, it is significant that the chloride process is in effect the starting process for metal production, as an intermediate product TiCl_4 is produced. Sulphate process intermediates are not utilized for metal production.

3.0 WORLD PIGMENT CAPACITY

3.1 Chloride vs Sulphate Process

The trend toward the chloride process is easily understood if the two processes are compared on the basis of waste production, process efficiency and product quality. Pigment capacity by process is shown in Figure 4.

Sulphate Process Using Primary ilmenite as the main feedstock creates 3 to 4 tonnes of liquid acid and solid recycled. (Although the Du Pont copperas (iron sulphate) waste per tonne of pigment.

Chloride Process Solld waste is not a problem and the main by product, chlorine, is process produces significant amounts of liquid ferric chloride waste which is pumped into disposal wells).

The conversion efficiency is 85 to 90%

Product quality is affected by the production of both rutile and anatase forms of pigment.

Product quality is maintained at a high level with the production of rutile grade pigment only.

The conversion efficiency is 95%

(The Du Pont process has a 92% efficiency rating).



Figure 4. Pigment Capacity by Process.

Chloride process capacity should exceed sulphate process capacity by 1995 because of environmental and cost factors.

3.2 Regional Pigment Capacity

The heavy dependence of Western Europe on sulphate process pigment production is seen in Figure 5.

The European Economic Community may see a more rapid move to modify or even close sulphate based capacity in Western Europe or convert it to the chloride process. In Japan, the authorities are also taking a tough line with little new capacity permitted unless it replaces sulphate process pigment plants.



Sulphate Process

Chloride Process

Figure 5. Pigment Capacity By Region, 1988

4.0 WORLD TITANIFEROUS FEEDSTOCK PRODUCTION

Australia dominates the world supply of high titanium dioxide feedstocks with major production coming from Renison Goldfields, Consolidated Rutile and Westralian Sands.

4.1 Feedstock Supplies to Chloride Process Pigment Plant

Renison is the world's major supplier to chloride process pigment plants. As Figure 6 shows, Renison Goldfields supplies 25% of the world's secondary ilmenite and 36% of the world's synthetic rutile. The Company is also a major supplier of natural rutile, sharing this position with Consolidated Rutile, Sierra Rutile (SRL) and Richards Bay Minerals (RBM). Pigment producers, Du Pont, SCM and Kerr-McGee (KMC) have large amounts of tied production of secondary ilmenite and synthetic rutile.



Figure 6. Feedstock Suppliers to Chloride Process Pigment Plants.

4.2 Feedstock Suppliers to Sulphate Process Pigment Plants

The supply of titanium dioxide feedstocks to pigment plants using the sulphate process is dominated by the slag producers (see Figure 7). QIT and Richards Bay Minerals share 88% of the slag market while NL Industries is the main supplier of primary ilmenite from its hard rock mine at Tellnes in Norway. Australian mineral sand producers, Westralian Sands, Cable Sands and Renison Goldfields are also significant suppliers of primary ilmenite.



Figure 7. Feedstock Suppliers To Sulphate Process Pigment Plants

4.3 Increasing Australian Production

In 1990 when Cooljarloo production reaches the market and Australian production will account for 68% of secondary ilmenite production, 67% of synthetic rutile production and 67% of natural rutile production. (These figures are nett production figures, i.e. ilmenite production of 440,000 tpa from Cooljarloo is adjusted down by 210,000 tonnes used in synthetic rutile production feedstock).



Figure 8. World Production 1991

This dominance in output highlights Australia's pivotal role in future supply to both the pigment industry and the titanium metal market.

5.0 THE COOLJARLOO INTEGRATED PROJECT

The typical extraction and beneficiation path for titaniferous feedstocks is illustrated by the integrated Cooljarloo project. (The total project concept is shown in Figure 9).

5.1 Cooljarloo Mine And Wet Concentrator

The Cooljarloo Orebody is located 25 kilometres inland from the present coastline and 170 kilometres north of Perth, the capital city of Western Australia.

Proven and probably reserves of 569 million tonnes with an average grade of 3.2% and total content of 18.3 million tonnes of heavy minerals put Cooljarloo in the major deposit class.

The typical heavy mineral assemblage is 60% ilmenite, 4.4% rutile, 9.1% leucoxene, 11.2% zircon and 0.6% monazite. Titanium dioxide contents of the titaniferous feedstock minerals are on average, ilmenite 62%, rutile 96% and leucoxene 25%, although the latter fraction encompasses a very broad range.

Mining is achieved with a low unit cost, bulk tonnage floating dredge operation. The bucket wheel suction dredge supplies sand to a feed preparation system of trommels to remove oversize material and hydrocyclones to remove light weight clay rich slimes. From feed preparation, the sand slurry is fed into a spiral concentrator which relies on differential specific gravities to separate valuable heavy minerals from the silicate gangue.

Treatment is via a three stage series of spirals which produce increasing concentration of heavy minerals with each stage up to approximately 92% heavy minerals in the final dewatered concentrate. The sand and slimes tailings from the concentrator are returned to the dredge pond for disposal. Any material with an SG less than 3 is separated in the cyclones and spirals then returned to the mine as waste.

5.2 Dry Separation Plant

In preparation for dry separation processing, surface contaminants are removed from the heavy mineral grains by several stages of attritioning.

The clean, dry, heavy mineral concentrate is selectively sorted into conductors, (ilmenite, rutile and leucoxene) and non-conductors, (zircon and monazite) by high tension electrostatic separators.

Differing magnetic properties are used to split the conductive minerals into individual constituents. The non-conductors are processed through magnetic and wet gravity separations to produce zircon, a monazite concentrate and a non-valuable heavy mineral fraction.

Crossbelt magnetic separators are used to separate materials of greatly different magnetic susceptability and induced roll magnetic separators are applied for more subtle differentiation.

5.3 Synthet1c Rut.11.e Plant

The high TiO_2 content feedstocks, rutile and some grades of leucoxene, are fuel for the chlor1de process pigment plants. Relatively minor sources of ilmenite are suitable for direct chlorination although ore grade ilmenite deposits are in abundance compared with sources of natural rutile.

Ilmenite can be utilised in the chloride pigment process by first upgrading it to synthetic rutile. For Cooljarloo ilmenite, the Improved Becher Process achieves an increase in TiO_2 content from 62% to 92% by transforming it to synthetic rutile through the removal of iron and manganese oxides.

The Becher process reduces iron and manganese oxides ti metallic or a sulphidised form in a sulphurous atmosphere, high temperature, coal-fuelled rotary kiln. The process also produces partial reduction of TiO_2 to Ti_2O_3 and creates a porous crystal structure in the reduced ilmenite.

The iron manganese sulphide is leached from the ilmenite grains with weak sulphuric acid.

Dissolution of the metallic iron phase takes place in an aerated, aqueous bath using an ammonium chloride catalyst. The metallic iron diffuses through the porous network of the ilmenite to the grain surface where it is oxidized to insoluble Fe_2O_3 . The remnant grain with the iron and manganese salts removed is synthetic rutile with approximately 90-94% TiO₂ content.

Precipitated iron oxide is separated from synthetic rutile in hydrocyclones. The product is subjected to a final leaching in weak sulphuric acid to remove manganese and any residual metallic iron before washing and drying to a saleable form.

5.4 Chloride Process Pigment Production

Rutile, high grade leucoxene, synthetic rutile and high grade titania slag are suitable feeds for chloride process pigment plants. In the output of waste material, the chloride process is much more environmentally acceptable to the alternative sulphate process.

In the Cooljarloo example, synthetic rutile is reacted at high temperature with petroleum coke and chlorine gas in a fluid bed chlorinator. The reaction produces metal chlorides and other gas. Titanium tetrachloride (TiCl₄) is separated from the gas stream and condensed to a liquid which is distilled to remove impurities.

Pure titanium tetrachloride can be used to produce titanium dioxide pigment or titanium metal products.

The oxidation process burns oxygen and pure TiCl_4 , activated by an aluminium chloride catalyst, to produce TiO_2 particles and chlorine gas. The solids and gases are separated before the plant is further treated to enhance its opacifying qualities and the gas is recycled.

Titanium metal can be produced using the Hunter, Kroll or Electrolytic Ginatta processes. The Hunter and Kroll processes react $TiCl_4$ with sodium and magnesium respectively to produce titanlum metal and chlorides. The Electrolytic Ginatta process involves electrolysis of $TiCl_4$ to produce metal and chlorine gas.

CONCLUSION

Many titaniferous metal deposits have been located around the world, however, there are two major constraints for further development:

1. The grade of the deposits are dropping from 9% to 12% mined 10 years ago to as low as 3% to 5%.

The lower grade mines need to be extracted using highly mechanised dredging methods which are capital intensive and will require an abundance of water for ponds and processing.

 Environmental constraints are the biggest factor against new developments because most deposits are near coastlines with more delicate ecological balances and near centres of population.

The mines with lower grades need to strip vegetation over larger areas. However, with proper rehabilitation techniques the land can be readily returned for agricultural use in better condition than the usual mineral and nutrlent deficient soil found prior to mining. Over the next 20 years there are sufficient known titaniferous mineral deposits to keep supplying the world's needs. Any rapid growth in titanium metal production is unlikely to be restricted by production of titanium tetrachloride or titaniferous minerals.

COOLJARLOO MINE AND WET CONCENTRATION







CHLORIDE PROCESS Ticl4 PRODUCTION & USE

