

Synthetic Rutile Production from Murray Basin Ilmenite by the Austpac ERMS Process

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A paper presented at the Murray Basin Mineral Sands Conference, 21-23 April 1999, Mildura, Victoria, Australia, and published in AIG Bulletin No 26.

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1. Introduction

Two commercial systems are in current use for production of the world's synthetic rutile, namely:

The well-documented Becher process, as used extensively in Western Australia, and

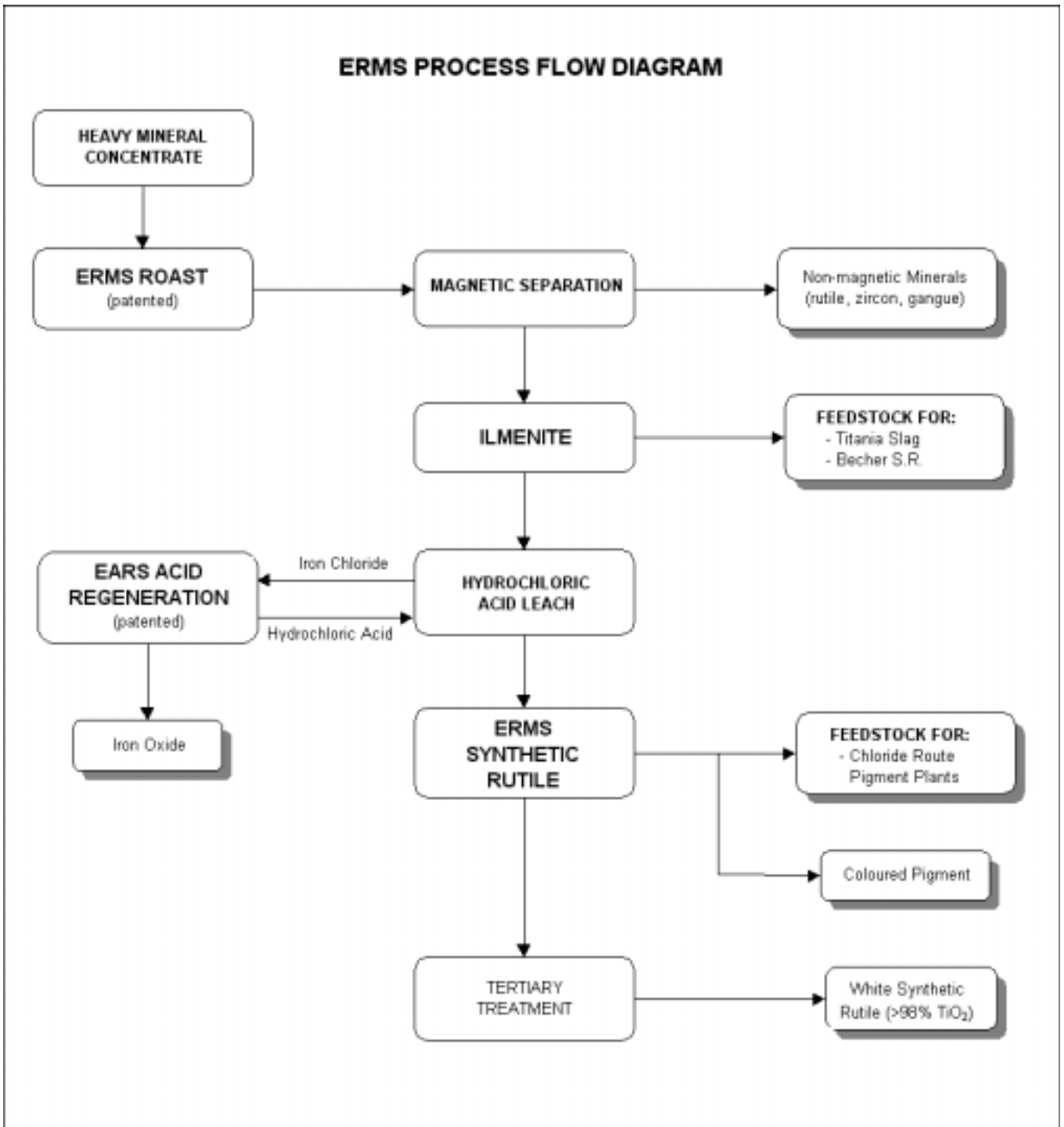
The Benilite process, used in India, Malaysia and the USA, which involves leaching treated ilmenite with hot hydrochloric acid under pressure.

Austpac Resources N.L. has developed an atmospheric-pressure hydrochloric acid leaching process, which has been successfully operated at pilot-plant scale on a wide range of ilmenite types, including some from the Murray Basin. In every case it has been possible to make a low-chrome, high-grade synthetic rutile of 95% TiO₂ content or higher. When this leaching system is coupled with Austpac's proprietary Enhanced Roasting and Magnetic Separation (the "ERMS" Process) short leaching cycles are possible without the need for the aggressive conditions and high capital cost associated with pressure leaching.

2. Process Description

2.1 Heavy Mineral Concentrate Production

The production of HMC (Heavy Mineral Concentrate) follows conventional wet gravity separation methods and is not shown on the ERMS Process Flow Diagram below. The ERMS roasting process can tolerate quite low-grade feeds, but equipment size and fuel use dictate that some further upgrading from a spirals-type concentrate is warranted. This may be done using a conventional WHIMS (Wet High Intensity Magnetic Separator) followed by drying and separation of a 70% to 80% ilmenite concentrate, using a rare-earth magnetic drum. Obviously, other processing options are available.



2.2 Roasting and Magnetic Separation

The aim of the roasting stage is to condition the ilmenite so that leaching in hydrochloric acid will selectively remove iron and other impurities from the titania fraction. This requirement can be met with suitable control of the operating parameters, some of which are covered by patent.

Roasting is carried out in a segmented fluid bed roaster. Optimum operating parameters have been determined for a large number of different ilmenites by statistical modelling, together with extensive pilot plant operation in both batch and continuous systems.

There are many aspects of this operation which are confidential but it can be said that:

Control is straightforward.

A wide selection of suitably modified commercial roasters can be used.

Temperatures are moderate and may range from 750°C to 850°C, depending to some extent on the type of feedstock.

Average residence times vary from 30 minutes to 2 hours.

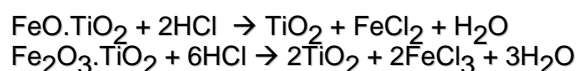
A wide variety of fuels may be used.

Combustion conditions are sub-stoichiometric.

Roasting is followed by a magnetic separation stage to remove gangue minerals. The ERMS process can be particularly well applied to the removal of chromite, and at the same time give a high ilmenite recovery and is therefore well adapted for the handling of Murray Basin high-chromite ore types.

2.3 Hydrochloric Acid Leaching

ERMS-roasted ilmenite is highly reactive to hydrochloric acid leaching. The leach reactions may be simplified to the following:



Any oxides of calcium, magnesium, manganese, aluminium etc. that occur as impurities within the ilmenite are similarly dissolved. Most of the TiO₂ is insoluble. The small fraction that dissolves initially is precipitated by hydrolysis as hydrated oxychlorides, and converted later to TiO₂ by calcination.

The rate of reaction is very important, as the capital cost of leach vessels is a significant proportion of the total capital cost. This reaction rate is influenced by:

Heat treatment parameters eg roasting time, temperature.

State of oxidation of the roasted ilmenite.

HCl concentration.

Concentration of iron chlorides.

Temperature.

The first two factors are controlled in the roasting stage. The aim is to have a low Fe(III) content, consistent with the need for both good magnetic properties and good leachability.

HCl concentration is normally limited to a maximum of 20%, due to the formation of an azeotrope of approximately this composition during regeneration. However, Austpac has developed the Enhanced Acid Regeneration System (the "EARS" Process), which is capable of economically producing acid of super-azeotropic concentrations of up to 33% HCl.

A high concentration of iron chlorides in the leachate is beneficial but solubility of the chlorides and viscosity of the solution impose limitations which must be taken into account.

The reaction rate is very temperature sensitive. The leaching section of the ERMS process operates at about 105°C, which is just below the boiling point of the leachate at sea-level ambient pressure. Higher temperatures will lessen leaching times but for this, pressure operation is required. The well-known Benilite process is an example of this technique. However, pressure leaching introduces other

problems, such as the need for heavy-walled vessels and special seals, which are avoided in the ERMS system. Pressure leaching is unable to remove as much iron in the ilmenite so the synthetic rutile product has less TiO_2 than that made by the ERMS process.

ERMS leaching is carried out in steam-heated fluid-bed reactors. With this style of reactor, agitation is very gentle and formation of slimes by attrition is minimised.

It is important to consume as much HCl from the leach liquor as possible to lessen the evaporative load in the energy-intensive acid regeneration reaction. This is most readily achieved with multi-stage counter current operation. Even so, some excess acid above stoichiometric requirement is needed for effective iron dissolution.

Liquid-solid separation between stages is achieved very simply by settling and decantation.

Typical leaching parameters for a Murray Basin ilmenite are:

Feed ilmenite	35% Fe_2O_3 equivalent, 61% TiO_2
Feed acid concentration	25% HCl (by mass)
Synthetic rutile product	0.5% Fe_2O_3 , 97% TiO_2
Spent acid (leachate)	5% HCl (by mass)
Temperature	105 °C
Overall cycle time	4 hours

2.4 Filtration

Liquid-solid separation is carried out on a four-stage belt vacuum filter. The first stage separates the mother liquor and the remaining three stages are used for counter current cake washing. The spent wash liquor is then used for HCl absorption in the acid regeneration section.

2.5 Calcination

The washed product from the filter is dried and calcined in a fluid bed. This operation hardens the now porous grains by incipient sintering and removes residual hydrochloric acid and water, a proportion of which is chemically combined with the TiO_2 in the product as complexes.

The temperature used for calcination will depend on the end use of the synthetic rutile product ie. whether it is to be used as a chlorinator feedstock or to be finely ground for direct use as a coloured pigment, as colour is somewhat dependent on calcination temperature.

Following calcination, magnetic separation may be used as an optional step to remove the small fraction (nominally 2-3%) of difficult to leach material and any residual gangue minerals. An assay of a typical magnetic fraction is given in column 3 of the Appendix.

2.6 Synthetic Rutile Products

Calcined synthetic rutile from one of the Murray Basin ilmenites tested so far had an analysis similar to that given in Table 1 below. It contained less than 0.5% Fe_2O_3 equivalent and is very low in other impurities which could be considered deleterious to a Chloride Process pigment TiO_2 plant.

The product was pale yellow in colour. Similar products overseas have been micronised for a limited market as off-colour pigments or pigment extenders where colour is not critical (eg Hitox and Uttox pigments).

Table 1: Typical Raw Material And Product Assays

Component (%)	Ilmenite Feed	Calcined Synthetic Rutile
TiO ₂	60.8	97.2
Fe ₂ O ₃ *	35.0	0.4
SiO ₂	0.94	1.4
Cr ₂ O ₃	0.15	0.1
ZrO ₂	0.01	<0.1
Al ₂ O ₃	0.76	0.4
CaO	NA	Trace
MgO	1.82	0.1
MnO	1.13	Trace
V ₂ O ₅	NA	ND
P ₂ O ₅	0.06	0.1
Nb ₂ O ₅	NA	0.2
U (ppm)	8	ND
Th (ppm)	109	ND

*Total iron as Fe₂O₃

NA = Not analysed

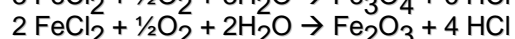
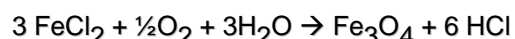
ND = Not detectable (below limits of detection)

3. EARS Hydrochloric Acid Regeneration

The distinct advantage of using hydrochloric acid rather than as a leachant (for example), sulfuric acid is that hydrochloric acid may be readily regenerated from iron chloride liquors. Sulfate liquors are much more difficult to regenerate and are typically wasted, such as in the Sulfate TiO₂ process.

There are several possible process routes for the regeneration of hydrochloric acid, but commercially, the most popular is by pyrohydrolysis. The EARS system is based on this technique.

The predominant reactions are:



Other chlorides (except calcium) behave similarly. Good recoveries are achieved, but some make-up acid will be required.

In systems other than EARS, pyrohydrolysis is accomplished by spraying or injecting the feed liquor into a roaster, operating at about 800°C, and absorbing the HCl off-gas in water to make hydrochloric acid. Such systems have long been used in the steel industry to regenerate pickle liquors and have reached a high level of performance and reliability. However there are upper limits to the capacity of such units and thermal efficiency is low, due to the large volumes of diluent nitrogen from the combustion air, compounded because both the nitrogen and evaporated water are heated to 800°C in the roaster, with subsequent heat loss and volume expansion. For the regeneration of liquor, produced by leaching ilmenite, multiple reactors are required if standard technology is used, because the volume of liquor generated is much greater than that of pickling lines in steel mills.

To overcome these problems, it was decided to remove the bulk of the water content of the leachate by pre-evaporation at a low temperature (approximately 130°C) using a technique borrowed from the fertilizer industry, namely, by using a combination of pelletiser and rotary drier. The dry iron chloride pellets produced by this method are then fed to a fluid bed roaster.

Pyrohydrolysis is carried out in a fluid-bed. In these units the solid oxide discharge is in the form of small pellets as opposed to the fine powder of spray systems. This is a decided advantage when it comes to subsequent handling and disposal.

Other acid regeneration processes use gas or fuel oil for energy. The EARS process has the advantage of being adaptable to most types of fuel, and cost will dictate the choice. Where coal is cheaper than oil or gas, it can be used for both pellet drying and pyrohydrolysis. For the roaster, coal and iron chloride pellets are mixed and fed directly to the fluid bed.

The gases exiting the fluid bed are cleaned and absorbed, according to normal practice. Rinse water from the filtration stage can be used as an absorbent. The product acid from steel-pickling acid regeneration plants is normally 18% to 20% HCl (by mass) which is a limitation imposed by the composition of the HCl - H₂O azeotrope. However a feature of the Austpac EARS process is that super-azeotrope concentrations of up to 33% HCl can be readily made, if required. This leads to a lower production cost than when sub-azeotropic acid is used, because of more rapid leaching time and smaller vessels. For low-iron, high-titania Murray basin ilmenites, acid strength is not a critical parameter as leach cycle times are only short duration. Testwork carried out so far has been based on the use of 25% HCl.

4. Conclusions

The integrated Austpac ERMS/EARS technology offers significant advantages in the production of synthetic rutile and TiO₂ pigments, such as:

Easy separation and very high recovery of ilmenite to produce a high quality concentrate from any HMC source. It can handle refractory ilmenites, chrome-contaminated concentrates and other problem ores. Over 50 ilmenites from around the world, including samples from the Murray Basin, have now been successfully tested.

Capital and operating costs are more than competitive with other synthetic rutile processes.

Regeneration of hydrochloric acid by the EARS process is cost effective. It has about half the capital cost and two thirds of the operating costs of other regeneration systems. There are substantial environmental benefits. The only solid waste product is pelletised iron oxide which can be sold to a steelworks or disposed of as inert landfill.

The acid leach removes radioactive and other deleterious elements from ilmenite and fixes them in the waste iron oxide pellets.

Engineering design and capital and operating costs have been completed for a number of locations and scenarios. From the available data bank already generated it can be confidently predicted that any proposal for a plant based on Murray Basin ilmenite would prove a competitive alternative to other synthetic rutile processes.

Acknowledgements

The author wishes to acknowledge the support and encouragement given in the development of the ERMS and EARS processes and the preparation of this paper by:

Austpac Resources N.L., Sydney, NSW
The University of Newcastle Research Associates Ltd, Newcastle, NSW
RZM Pty Ltd

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