

The Austpac ERMS and EARS Processes for the Manufacture of High-Grade Synthetic Rutile by the Hydrochloric Acid Leaching of Ilmenite¹

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ABSTRACT

Austpac Resources' proprietary 'Enhanced Roasting and Magnetic Separation' (ERMS) and 'Enhanced Acid Regeneration' (EARS) processes have been developed for the production of very high-grade synthetic rutile for the feedstock market for the chloride TiO₂ pigment process.

Ilmenite ore is roasted at temperatures in the range of 800°C to 1,000°C to selectively magnetise the ilmenite fraction so that gangue minerals may be easily removed. Roasting also enhances the subsequent leaching operation by activation of the iron component of the ilmenite whilst at the same time rendering the titania fraction insoluble.

Iron and other impurities are removed by leaching at atmospheric pressure with near boiling, 25 mass %, hydrochloric acid. The leached solids are filtered, washed and calcined to yield a synthetic rutile of 97% (or higher) TiO₂ grade.

Hydrochloric acid is recovered from spent leachate by evaporation and pyrohydrolysis, to yield a super-azeotropic acid. The fuel used can be gas, oil or coal, depending on local economics.

A pilot plant has been successfully operated for several years, using many types of fuel and ilmenite feedstock. A new coal-fuelled demonstration plant is now in the final design stage, to utilise ilmenite sourced from India and some of the emerging heavy mineral producers in Australia's Murray-Darling Basin.

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INTRODUCTION

The mineral ilmenite is primarily an iron titanate, which in the natural state varies somewhat in the FeO, Fe₂O₃ and TiO₂ content in individual ores. It is the primary raw material for the manufacture of a range of electrothermal slags and synthetic rutiles, for use as feedstocks in the manufacture of titanium dioxide pigments for the paint, plastics and other industries.

For many years synthetic rutile has been manufactured in Western Australia by the well-known Becher Process (1), which involves the reduction of the iron component to the metallic form and its subsequent removal as a type of rust in air-sparged agitated vessels. This process performs well with ores that are high in titania and low in iron oxides and when a reactive low rank coal is used as a reductant.

By comparison, the Benilite (2), Laporte (3) and Murso (4) and similar processes utilise selective leaching with hydrochloric acid as the means of removing the unwanted iron. Hydrochloric acid leach systems are more tolerant in their fuel and feedstock requirements than the Becher process and are capable of producing a higher quality synthetic rutile. However only the Benilite process has been commercially developed to any extent and all existing plants are somewhat aged. Austpac Resources N.L. anticipated a need for a more modern and more cost effective hydrochloric acid leach system and this paper describes the development and application of such a process.

In the late 1980's, Austpac became involved in the evaluation of substantial ilmenite deposits at Westport on the west coast of the South Island of New Zealand. Westport ilmenite was known to be difficult to separate because individual grains contain numerous silicate mineral inclusions, and the heavy mineral concentrate contained a significant proportion of free garnet. The garnet has a density and magnetic-electrical properties similar to the ilmenite, and consequently is difficult to remove by conventional mineral sands beneficiation procedures.

An extensive literature survey on the thermal treatment of iron-bearing minerals to enhance their magnetic properties was undertaken in parallel with detailed testwork with a laboratory-scale and pilot plant-scale fluid bed roasters. This yielded a technique to selectively magnetise ilmenite to the extent that very easy separation from garnets and other gangue minerals, with high recovery rates, was now possible. The process was designated the 'Enhanced Roasting and Magnetic Separation' (ERMS) process.

Testwork also revealed that under certain conditions roasting also rendered the iron and other non-silica impurities selectively leachable in hydrochloric acid, to produce a high quality synthetic rutile. Subsequent research was directed at improving leachability, with considerable success. As previously indicated, hydrochloric acid leaching of ilmenite was not new but Austpac developed some effective in-house techniques to significantly reduce costs compared with other systems. The most important of these was the use of atmospheric pressure leaching and the patented 'Enhanced Acid Regeneration' (EARS) process (5).

Since then, extensive bench scale and pilot plant test work has been carried out on many more ilmenite types, ranging from the so-called 'fresh' (high-iron) ilmenites to 'weathered' (low iron) ilmenites, as well as high-chrome and very fine-grained ilmenites, all of which have been

successfully processed. Present development work is centred on ilmenites from Orissa State in India and from the newly explored deposits of Australia's Murray-Darling Basin.

Concurrent with this pilot plant research, design and costing by an independent contract-engineering group have been carried to the point where it can be confidently predicted that the economics of the overall system are very sound, and planning for the first production-scale unit is well advanced.

The generalised flow sheet given in Figure 1 above illustrates the major steps in the production of synthetic rutile using Austpac technology, which will be described in the text.

HEAVY MINERAL CONCENTRATE

Heavy mineral concentrate production follows conventional wet gravity and dry mill separation methods and is not shown on the flowsheet. The ERMS roasting process can tolerate low-grade HMC feeds, but equipment size and fuel use dictate that some further upgrading from a wet gravity (spirals-type) concentrate to an impure ilmenite is warranted. This may be done using a conventional WHIMS (Wet High Intensity Magnetic Separator) (6) followed by drying and separation of a 90 % (or so) ilmenite concentrate, using conventional 'dry mill' techniques and rare-earth magnetic separators.

ROASTING

The aim of the roasting stage is to:

- Selectively and uniformly magnetise the ilmenite fraction of the ilmenite concentrate, so that a pure ilmenite can be easily extracted by dry magnetic separation, with high recoveries;
- Condition the ilmenite so that leaching in hydrochloric acid will readily remove iron and other impurities from the titania fraction.

Both these requirements can be met with suitable control of the operating parameters, some of which in the ERMS process are covered by patent (7)

Roasting for acid leaching is carried out in two fluid bed stages, operating in tandem. In the first stage, the ilmenite concentrate is heated in an oxidising atmosphere so that almost all of the iron is converted to the trivalent state. In the second stage, the trivalent iron is reduced to the divalent state, in which form it is very readily leached. The titania fraction is rendered virtually insoluble when the ilmenite is roasted in this manner.

Oxidation / reduction roasting as developed by Austpac employs operating temperatures of over 1000°C, with a total residence time of between 2 and 3 hours. The reduction stage is controlled to give a very high Fe (II) / Fe (III) ratio in the roasted product, as in this form it is most readily leached. Coal (of any locally available type) is normally the preferred fuel but the process can utilise gaseous or liquid fuels if these are cost effective

Different ilmenite types require specific operating conditions for optimum performance and it is first necessary to determine these parameters by statistical modelling, together with extensive pilot plant operation in both batch and continuous systems. The roasting conditions are critical to the success of the subsequent leaching operation, but once established, continuous control of the process is not difficult to maintain.

Ilmenite that has been reduced in this manner is very reactive and care is needed to ensure that the product is cooled in the absence of air when discharged from the roaster.

Excess Char Removal

Some excess char is produced when coal is used as a reductant. This and the bulk of any ash are separated from the cooled product on a vibrating screen. The aperture of this screen depends on the size of the ilmenite particles and is nominally 0.5 mm. The small fraction of char passing through the screen is removed later in the magnetic circuit. A portion of the unburnt char is recycled to the roaster, and the remainder is burnt as fuel for steam raising or acid regeneration.

Magnetic Separation

Reduced ilmenite is magnetically enhanced, so most of the remaining gangue and fine char particles are readily removed using a rare-earth magnetic separator. Any gangue minerals remaining after this, such as weakly magnetic chromite and garnets, are carried through the subsequent leaching stages and removed magnetically at the end of the system

LEACHING

Ilmenite that has been correctly roasted in the above manner can be readily leached in hot hydrochloric acid to remove almost all of the iron content and other unwanted impurities, including residual radio-actives, to leave a purified titanium dioxide residue.

Hydrochloric acid has been chosen as the reagent in preference to, say, sulfuric acid because it may be readily recovered from the spent leach liquor, and not give rise to unwanted by-products.

The main reaction during leaching may be simplified to the following:



Gangue minerals containing calcium, magnesium, manganese, aluminium etc. are similarly dissolved. Due to roasting, most of the TiO_2 is insoluble although a small fraction dissolves initially and is re-precipitated later by hydrolysis.

Achieving rapid leaching is very important, as the cost of leach vessels is a significant proportion of the total capital cost. The following are the most important parameters affecting this:

- Roasting time, temperature and oxygen potential;
- State of oxidation of the roasted ilmenite;
- HCl concentration;
- Concentration of iron chlorides in the leach liquor;
- Leaching temperature.

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

Hydrochloric acid concentration is very important, because not only does it affect the reaction rate, but it also has a significant influence on the overall water balance and fuel usage. In the ERMS Process, super-azeotropic (i.e. above 20%) is used, as this can be readily manufactured in the EARS acid regeneration process.

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

The leaching rate is very temperature sensitive. The ERMS process operates at about 105°C leaching temperature, which is just below boiling point of the leach liquor at ambient sea-level pressure. Higher temperatures will lessen leaching times but then pressure operation is required. This is considered undesirable because pressure operation requires the heavy-walled vessels and special seals such as are used in the Benilite Process (2) referred to above. In the ERMS Process the need to shorten the leaching cycle is more readily achieved by detailed attention to effective roasting conditions.

Contrary to what might be expected, the leaching rate is not sensitive to particle sizing. The progress of the reaction does not follow the classical ‘shrinking core’ model but tends to follow lines of micro fractures induced by the prior roasting regime

Leaching in the ERMS Process is carried out in steam-heated, liquid-solid, fluid-bed batch reactors. With this style of reactor, agitation is very gentle and formation of slimes by attrition is minimised. This is important because the end use of synthetic rutile, namely chlorination in fluid beds, demands a product with minimum fines in the minus 90µm range. Table 1 below illustrates the size of a typical feed ilmenite and the synthetic rutile produced from it by leaching, from which it can be seen that there has been minimum size degradation during the leaching operation.

Table I –Particle Sizing of Feed Ilmenite and Synthetic Rutile Product

Sieve Aperture (µm)	Cumulative % retained	
	Ilmenite to leaching	Synthetic rutile product
63	99.4	100
90	98.6	99.4
125	90.6	93.5
180	57.1	51.9
250	18.8	11.7
355	1.7	0.8
500	0.0	0.0

The graph below (Fig.2) illustrates the progress of a typical leach cycle. The pertinent points (with the particular type of ilmenite used) are:

- Leaching is virtually complete in three hours;
- The excess acid requirement is quite modest;
- 25% (i.e. super-azeotropic) acid is used as a leachant.

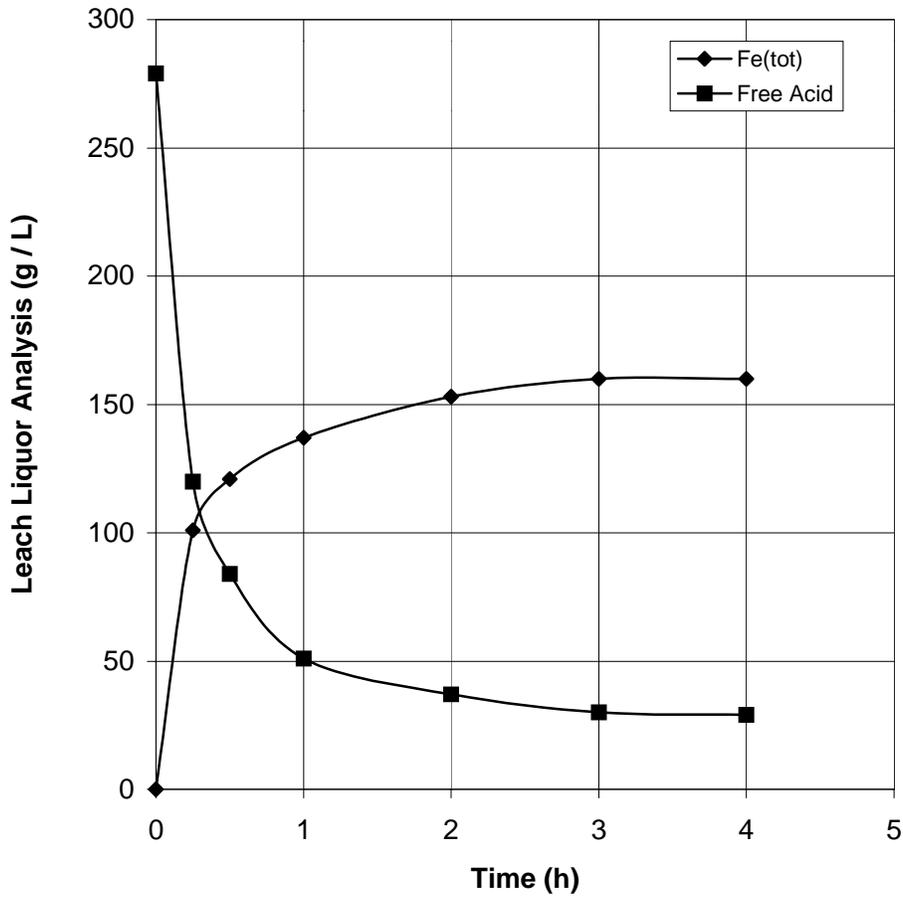


Figure 2 - Leach Cycle Curve for a Typical Ilmenite Roasted and Leached according to Parameters Determined by Austpac ERMS/EARS Technology.

The feed and product assays pertaining to Figure 2 above are given in Table II.

Table II – Chemical Analysis of a Typical Ilmenite and Product Synthetic Rutile

Component	Ilmenite (mass %)	Synthetic Rutile (mass %)
TiO ₂	50.4	97.3
FeO	34.1	0.0
Fe ₂ O ₃	12.1	1.08
Al ₂ O ₃	0.55	0.13
SiO ₂	0.76	0.79
MgO	0.67	0.02
MnO	0.61	0.01
P ₂ O ₅	0.01	0.02
CaO	0.04	0.01
Nb ₂ O ₅	0.11	0.23
V ₂ O ₅	0.28	0.02
ZrO ₂	0.04	0.01
Cr ₂ O ₃	0.09	0.02
Other	0.23	0.38
Th (ppm)	40	6
U (ppm)	<5	<5
Normalised	~100	

It is significant that the acid leach removes most of the radioactive and other deleterious elements from the ilmenite feed, which are subsequently fixed in the iron oxide pellets during acid regeneration.

FILTRATION, WASHING & CALCINATION

Liquid-solid separation is carried out on a four-stage vacuum belt filter. The first stage separates the mother liquor and the remaining three stages are used for cake washing.

The wash liquor from filtration is used for HCl absorption in the acid regeneration section. The amount of wash water used determines the acid concentration that can theoretically be reached during regeneration and also determines the amount of fuel that has to be used for its subsequent evaporation. In the ERMS/EARS processes this quantity is closely controlled, enabling not only efficient cake washing, but the subsequent production of a super-azeotropic acid in the regeneration plant

The washed product from the filter is dried and calcined at around 800°C in a fluid bed system. This operation hardens the now porous grains by incipient sintering. It also removes residual

hydrochloric acid and water, a proportion of which is chemically combined with the TiO₂ as complexes.

Following calcination, high intensity magnetic separation is used to remove the small fraction (nominally 2%-3%) of difficult-to-leach material and any residual magnetic gangue such as garnets or chromite.

HYDROCHLORIC ACID REGENERATION

Austpac developed the patented EARS process (5) as a cost-effective route for the regeneration of hydrochloric acid from the leach liquors. There are several possible process routes for the regeneration of hydrochloric acid, but commercially the most popular is by pyrohydrolysis, and the EARS system is based on a variation of this technique. The predominant reaction is:



Most of the other metal chlorides present in the spent leach liquor (except calcium) behave similarly. Excellent recoveries are achieved but a minor amount of make-up acid is required.

The iron oxide is depicted in the above equation as being in the hematite form. In practice the product contains some magnetite.

In some systems (for example the Keram Chemie, Babcock, and Ruthner systems) pyrohydrolysis is accomplished by spraying or injecting the feed *liquor* into a roaster. The HCl off-gas is absorbed in water to make *sub-azeotropic* 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 as synthetic rutile production on any reasonable scale requires the regeneration of much larger quantities of acid than is normally the case with steel pickling and multiple train plants are required when normal standard sized units are employed.

This capacity constraint is largely caused by the superheating and subsequent volumetric expansion of both combustion gases and steam from evaporation of the feed liquor, when raised to the roaster operating temperature.

The EARS process overcomes this problem by removing the bulk of the water load by complete evaporation at a low temperature (approximately 140°C) in a separate fluid bed unit, thus avoiding much of the superheating and volumetric expansion of the off-gas. The *dry metal chloride pellets* produced by this method are then fed to a fluid bed roaster for pyrohydrolysis. A similar procedure was developed by Falconbridge (11) for the pyrohydrolysis of nickel chloride, the main difference being that in their case crystallisation and drying steps were employed rather than the single step fluid bed evaporation/ pelletising of the EARS process.

A further and major advantage of using a solid feed for pyrohydrolysis is that super-azeotropic acid can be produced (i.e. above 20 mass %), resulting in substantial fuel saving by minimising water load in the evaporator, and at the same time enhancing leaching rate.

The EARS process can be adapted to use most types of fuel, and cost will dictate the choice. Where coal is cheaper than oil or gas, it can be used for both evaporation and pyrohydrolysis.

It should be emphasised that although the process has some novel ideas, none of the equipment items used are novel in themselves. Iron chloride pyrohydrolysis has been practised in the steel industry for many years, and evaporation and pelletising of soluble salts is widely used in the manufacture of many types of fertilizer and other materials

The major components of the EARS Process are shown in Figure 3 below.

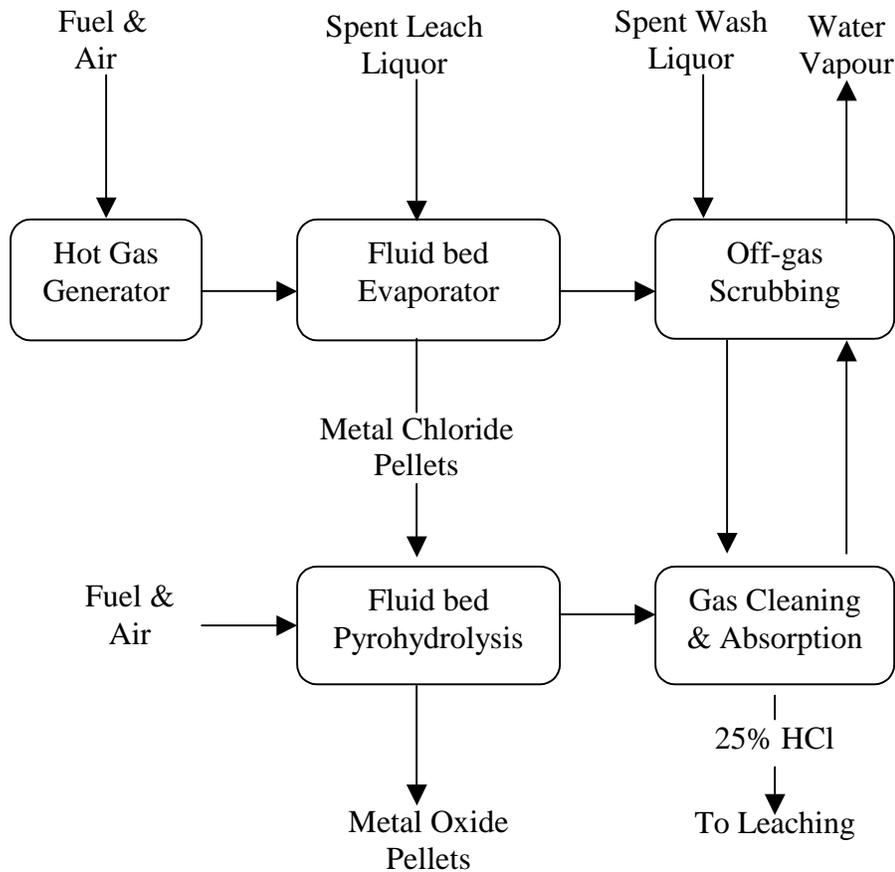


Figure 3 - Simplified Flow Diagram of the Austpac EARS Process.

Evaporation and Pelletising

The thermal energy for evaporation, in the form of hot gas, is generated externally in a fluid bed coal or other combustion unit, and fed to the fluid bed evaporator, which is maintained at 140°C bed temperature. Iron (II) chloride has a number of hydrates and at this temperature the water of hydration of the pellets is slightly less than the dihydrate. It is so adjusted to suit the excess water requirement of the subsequent pyrohydrolysis reaction.

Evaporator off-gas treatment consists of combined venturi scrubbing and evaporative quenching with spent leach liquor, followed by adiabatic absorption in packed towers. Absorption liquor comes from the leached solids wash water and from the tail gas scrubber. The weak acid liquor from this operation is fed to the pyrohydrolysis absorption train.

The pellets range in size from approximately 1mm to 3mm in diameter, in which form they are readily stored and handled.

Pyrohydrolysis

Pyrohydrolysis is carried out in a fluid bed. In these units the solid oxide discharge is in the form of small (0.5mm to 2mm diameter) pellets as opposed to the fine powder of spray pyrohydrolysis systems. This is a decided advantage when it comes to subsequent handling and disposal.

The reaction is carried out in the range of 800°C to 900°C i.e. low enough to avoid overt agglomeration in the bed by sintering, but high enough to give good kinetics.

The iron oxide pellets may be used as feed to a steel mill sinter plant, or as an inert landfill. Other applications are possible.

Acid absorption

The gases exiting the fluid bed are cleaned and absorbed, according to normal practice. Filtrate washings, other rinse waters, or even a proportion of spent leach liquor, can be used as an absorbent.

A distinct attribute of the EARS process is that super-azeotropic acid can be readily made, by virtue of water removal during the evaporation of the spent leach liquors. By comparison, the acid from steel-pickling acid regeneration plants is normally only about 18% HCl, this being a limitation imposed by the composition of an HCl-H₂O azeotrope at approximately 20 mass % HCl.

The use of superazeotropic acid leads to a much lower production cost than when sub-azeotropic acid is used, because of the more rapid leaching time and smaller recirculating acid volumes. The reduced acid volume also means there is less water to evaporate during each pass, which significantly lowers the fuel cost.

CONCLUDING REMARKS

The integrated Austpac ERMS and EARS technology for production of synthetic rutile has many advantages. These include:

ERMS

- It can produce a very high-grade synthetic rutile from any ilmenite;
- It can handle refractory ilmenites, chrome-contaminated concentrates and other problem ores. Over 75 ilmenites from around the world have now been successfully tested;
- Capital and operating costs are more than competitive with other synthetic rutile processes;
- Gas-solids fluid bed units are utilised for ilmenite roasting, synthetic rutile calcining and acid regeneration;
- Leaching is carried out at atmospheric pressure in a liquid-solids fluid bed reactor;
- Overall processing retention time is short, therefore equipment size per unit of capacity is small;
- The process is not fuel or ore specific;
- High-grade synthetic rutile (+97% TiO₂) is produced;
- High recoveries of ilmenite/TiO₂ are achieved;
- Zero liquid discharge is achieved.

EARS

- The process is not fuel specific. In addition to liquid or gaseous fuels, solid fuels, such as, coal or char can be used;
- Regeneration of hydrochloric acid by the EARS process is cost effective, due to reduced capital cost (based on large scale operation) and reduced operating cost (by using low cost fuels) when compared to the alternative processes available;
- There are substantial environmental benefits. The only solid waste is in the form of an oxide pellet, which can be disposed of as inert landfill. Any radioactive or deleterious elements are fixed within the solid waste. Other uses for the oxide pellets maybe found depending on the location, such as, feed to steel making, cement production or shot blasting;

- Super-azeotropic HCl acid concentrations can be produced which improves the leaching rate in the ERMS process, and significantly reduces the quantity of water recirculating with the acid, which in turn lowers the fuel requirement for regeneration;
- High recovery of HCl from spent leach liquors is achieved.

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