

WASTE MANAGEMENT - INTEGRATED TITANIUM DIOXIDE PIGMENT PLANTS

E. J. Anto

*The Kerala Minerals and Metals Limited,
Chavara, Kollam – 691 583, Kerala, INDIA.*

SYNOPSIS

The growing emphasis on environmental protection has necessitated rapid technological changes in the manufacturing processes in general and chemical industries in particular. Waste minimisation is relevant in this context. Waste minimisation is not new to the chemical process industries. Chemical industries always have aimed for the highest possible yields by recycling of materials and recovering co-products. The chemical process industries have now shifted their efforts from controlling discharges after they have been generated to prevent the generation of wastes itself. Waste minimisation is expensive, however, it is surely a lot cheaper than doing nothing. Titanium Dioxide Pigment industry is also not an exception to this. Waste minimisation through recycling and by-product recoveries has become the essential tool for the cost reduction and pollution control. Integrated Titanium Dioxide plants facilitate waste recycling in an effective way than the conventional Titanium Dioxide Plants. Integrated Chloride route process has distinct advantages to meet environmental demands.

INTRODUCTION

Ever since the commercialisation of chloride route process for the Titanium Dioxide manufacturing, it attracted newcomers in this field and some sulphate process plants also adopted chloride process. However, there is hardly any integrated plant producing Titanium Dioxide Pigment in the world with Mineral Separation facilities, Synthetic Rutile production, Titanium tetrachloride and Titanium Dioxide Pigment manufacturing in a single complex to utilise the advantages of total recycling. The Kerala Minerals and Metals Limited (KMML), Chavara is a unique set up in the field of TiO_2 Pigment Production having a complete integrated complex to produce TiO_2 Pigment from basic raw material – Beach sand. This facility in KMML is best suited for the prospective total recycling of effluent waste of one plant to another in the same complex to reduce effluent load and to increase the recovery efficiency. In this context, it may be appropriate to give a brief profile of KMML.

KMML – A PROFILE

KMML's integrated Titanium Complex situated at Sankaramangalam, Kollam consists of mainly two adjacent working units namely;

- i) Mineral Separation Unit (M S Unit)
- ii) TiO₂ Pigment unit (T.P.Unit)

Mineral Separation Unit (M.S.Unit)

In this unit, beach sand is mined from its own captive mines and various minerals viz., Natural Rutile. Ilmenite, Zircon, Leucoxene, Silliminite, Monazite, etc. are separated. Various separation techniques viz. screening, gravity separators, magnetic separators, high-tension roller separators etc. are used for this purpose.

Raw Ilmenite containing 58-60% TiO₂ is used as feed stock to TiO₂ pigment unit. Other minerals are sold to other industries to produce welding rods, refractories, glazing tiles, rare earth oxides etc.

TiO₂ Pigment Unit – T.P.Unit

This unit, which was commissioned in 1984, has the following main process plants:

Ilmenite Beneficiation Plant (IBP)

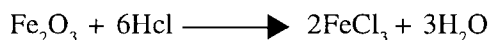
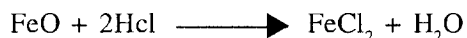
(BCA – Process) (Capacity 30000 TPA Synthetic Rutile)

In this plant, raw ilmenite from MS unit (containing 58-60% TiO₂, 23-25% Fe₂O₃, 10-12% FeO and other oxides like Al₂O₃, SiO₂, MgO, V₂O₅ etc) is upgraded to Beneficiated ilmenite or synthetic Rutile containing 90-92% TiO₂.

Raw ilmenite is first reduced in a rotary kiln to convert Fe₂O₃ to FeO using lecofiners at around 900°C.



The reduced ilmenite is leached with 18-19% Hcl to convert FeO to FeCl₂ and Fe₂O₃ to FeCl₃ in the soluble form.



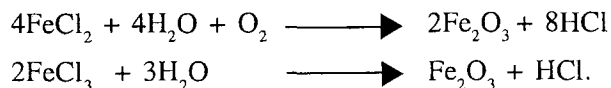
The leached ilmenite (insoluble TiO₂ rich) is washed, filtered and then dried in rotary calciner. The product, known as beneficiated ilmenite or synthetic rutile, containing 90-92% TiO₂ is used as feed stock to chlorination section of the Pigment Production plant.

The leach liquor, known as spent acid containing FeCl_2 , FeCl_3 and other chlorides is used as feed stock in Acid Regeneration Plant. The water containing 2-4% chlorides is also used in Acid Regeneration Plant for absorbing Hcl vapour.

Acid Regeneration Plant (ARP)

(Woodall Duckham .Process) (Capacity 25M³/Hr spent acid).

In this plant spent acid from IBP is regenerated to produce 18-18.5% Hcl. The spent acid is initially pre-concentrated and then spray roasted at 375-400°C using furnace oil where the hydrolization reaction takes place as follows:



The Hcl vapour is absorbed using the wash water from IBP to produce 18-18.5% Hcl, known as Recovered Acid which is reused for leaching in IBP.

The iron oxide is slurried and stored in large ponds.

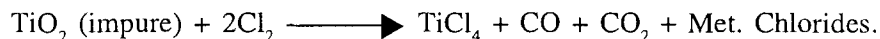
Pigment Production Plant (P.P.P)

(Kerr McGee chloride route Process) (Capacity 22000 TPA)

The pigment production plant consists of three sections as detailed below:

Chlorination Section (Unit 200)

In this section pure Titanium Tetra chloride (TiCl_4) is produced by chlorination of synthetic Rutile with calcianed petroleum coke and chlorine at about 1000°C in fluidized bed chlorinators.

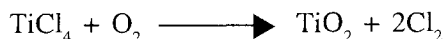


The products of reaction consist of crude Titanium Tetrachloride and metallic chlorides of impurities present in the ore along with unreacted ore and coke are cooled with TiCl_4 spray so that most of the impurity metallic chlorides are converted to solid state (AlCl_3 , FeCl_3 , FeCl_2 etc.) The unreacted ore and coke and solidified metallic chlorides are separated in cyclone separator and hydrolised with water (Excess filtrate water from the finishing section of PPP is used for this purpose). The slurry containing chlorides of metals in the liquid state and unreacted ore and coke in the solid state is pumped to effluent treatment plant where it is neutralized with hydrated lime and then pumped to settling pond. The clear water (neutral) after settling and polishing is pumped to sea.

The crude Titanium Tetrachloride is purified by distillation and impurities (mainly VOCl_3) are removed through continuous bleeding off the bottom residue. The pure TiCl_4 is pumped to oxidation section to produce Titanium Dioxide.

Oxidation Section (U-300)

In this section, TiO_2 pigment (rutile grade) is manufactured by the oxidation of preheated TiCl_4 with preheated oxygen.



The product, raw TiO_2 pigment, is slurried, dispersed and pumped to finishing section for final surface treatment. The Cl_2 gas, after cooling, dust cleaning and scrubbing with H_2SO_4 is recycled back to chlorination section.

Finishing Section (Unit 400)

In this section, raw TiO_2 pigment from oxidation section is screened, milled and treated with chemicals to impart the required surface properties to the pigment. The slurry is filtered, washed, dried and micronized to the required particle size and properties and then bagged.

The filtrate is collected in thickeners to recover traces of TiO_2 particles and overflow water is recycled back to chlorination section for the hydrolysis of the effluent.

Other facilities

To cater the requirements of process plants, KMML also have facilities like 50 TPD air separation plant, effluent neutralisation plant, Brine chilling plant, Storages for LPG, Cl_2 and other chemicals, utilities to supply air, water, steam, etc.

Waste Minimisation in Chemical Industries

As the World moves towards improving environmental standards and industrial practices, new processes are required to avoid the generation of environmental problem materials and deal effectively with existing problems. Industries have always aimed for the highest possible yields by recycling materials, recovering co-products and cleaning up the waste streams. Along with the safety, waste minimisation is without question the dominant technical issue facing the chemical industries. Environmental rules are providing some push for waste minimisation. But, the major impetus comes from public pressure in the form of lawsuits, protests, opposition to plant site etc.

Environmental pressures are changing the world -wide pigment market also. Initiatives to reduce waste in sulphate process are spurring Titanium Dioxide Producers to expand chloride process plants. Restrictions on heavy metals in pigments have proved a boom for

Titanium Dioxide Pigment which has become a safe alternative to other white pigments existed till the middle of 20th century. The Titanium Dioxide Pigment is said to be chemically inert and creates practically no user risks. This has resulted to the growth of Titanium Dioxide Pigment Industry. However, TiO₂ pigment manufacturing processes contribute varying degrees of waste generation. Pressures to reduce waste, have resulted in chloride plant expansions. The chloride process uses 50% less energy and produces 80% less wastes than the sulphate process.

Minimisation of waste from process industries can be broadly achieved by the following methods:

Reduction of the generation of waste at source itself

- i) By Process optimisation
- ii) By suitable additives like flocculent at the appropriate process stage to reduce fines generation which can be escaped from the process.
- iii) By conservation of process water which can cause dilution and volume increase of process chemicals used leading to overflow and waste.

Recycling of waste

- i) By recycling of dilute process streams containing process chemicals for absorption, washing and concentration build up.
Eg: Counter current washing in filters and enriching filtrate.
- ii) By recycling and regeneration of convertible ions into corresponding acids.
Eg. Chlorides to HCl, SO₄ to H₂SO₄ regeneration.

Production of by products

This can either be done by the process industry itself or through ancillary industries.

- Eg: 1. Alums from sulphate route TiO₂ industry.
2. Iron Oxide Pigment from Synthetic Rutile Plants.

WASTE GENERATION AND DISPOSAL IN TITANIUM DIOXIDE PIGMENT INDUSTRIES

Waste generation from Titanium Dioxide Pigment industries is basically derived from the impurities present in the basic raw material used in the TiO₂ manufacturing process. The types of waste generated from TiO₂ manufacturing are hence classified into three categories based on the process adopted.

1. Waste generation from Sulphate route Titanium dioxide Pigment Plants.
2. Waste generation from Ilmenite Beneficiation (Synthetic Rutile) Plants.
3. Waste generation from Chloride route Titanium dioxide Pigment Plants.

Waste Generation and disposal in sulphate route Titanium Dioxide Pigment Plants

Ferrous sulphate and spent sulphuric acid contribute major portion of waste from sulphate route Titanium Dioxide Pigment Plants apart from limited quantities of SO_2 and SO_3 emissions from the captive sulphuric acid plants. Approximately 3-4 tonnes of FeSO_4 and 8 Tonnes of spent acid is generated per Tonne, of Titanium Dioxide Pigment produced⁴ through sulphate process. Normally it is to be neutralised and discharged to sea. Developmental work to convert this SO_4 ions to sulphuric acid is still to be proven as a commercially viable process.

Although, conversion of this waste into by-product alums is being done recently by ancillary units, utilisation of such a large volume of the waste from Titanium Dioxide Pigment Industry may not be possible and hence to be treated prior to disposal.

Waste generation and disposal from Synthetic Rutile Plants

Synthetic Rutile is the basic feed stock for the chloride route Titanium Dioxide Pigment industries. The purity of Synthetic Rutile ranges from 92-96% Titanium Dioxide Pigment with 2-4% Fe_2O_3 as major impurity depending on the process. Basically the processes convert iron oxides into FeCl_2 or FeCl_3 and removed. In the waste generation view point it can be classified as follows:

- i) Process to convert iron into soluble FeCl_2 and FeCl_3 by Hcl leaching and regeneration of chlorides back into Hcl. In this case waste generation is mainly iron oxide.
- ii) Process to convert iron oxides into soluble chlorides form without regeneration of this chlorides. Large volume of acidic water containing chlorides is to be neutralized and disposed.
- iii) Process which convert chlorides of iron into by product.
- iv) Process with direct chlorination of iron oxides into chlorides as by product and separated.

Although the process is fuel oriented, KMML has adopted the first process and the waste generation is comparatively less. DCW Tuticorin, has process to produce Synthetic Rutile through the second process. Cochin Minerals Ltd., Cochin adopted the third process. Benchlor, Madras utilized the fourth processes (not in operation now).

In short, the success of efficient recycling of chlorides or conversion of chlorides into marketable products can bring down the waste and cost of production.

Waste generation from chloride Route Titanium Dioxide Pigment Production

Chloride route plants use synthetic Rutile as feed stock and hence the quantity of waste from such plants mainly depends on the purity of the feed stock. In this process, the impurities are converted into chlorides during the chlorination stage.

The chloride wastes mainly metallic chlorides are neutralized and lagooned. The total waste generation from chloride process is considerably less compared to sulphate route process since the raw material contains only 2-4% Fe_2O_3 as impurities.

Waste Minimisation through Integrated Chloride Route Process

Almost all chloride route Titanium Dioxide plants in the world are using synthetic rutile as feed stock which are produced in far away plants. The waste chlorides from such chloride route Titanium Dioxide plants are neutralised and disposed off. The waste generated from these plants contains unreacted ore and petroleum coke and metallic chlorides which can be utilised back in the synthetic rutile plants after separating the solid phase and the liquid phase of the effluent and enriching the chlorides to convert back to hydrochloric acid by regeneration process.

Vent gases leaving chlorination section producing Titanium Tetrachloride, contain TiCl_4 and Hcl vapour along with CO , CO_2 , N_2 etc. The uncondensed TiCl_4 and Hcl vapours also can be recovered by scrubbing to produce 20% Hcl. This can be used for leaching in Synthetic Rutile Plant.

The proximity of both synthetic Rutile Plant and chloride route pigment plant is hence a very useful factor for waste minimisation.

Excess filtrate water from the finishing section is generally used for hydrolysis of chlorination waste. This excess water can be utilised for the washing the iron oxide from Acid Regeneration Plant to make it acid free by product. Hence, the integrated chloride route Titanium dioxide Pigment production most prospective for the waste minimisation.

KMML's role in Waste Minimisation

KMML has already started utilising the facilities of having a totally integrated chloride route Titanium Dioxide Pigment Plant for the waste minimisation. Our goal is to reduce waste and emissions at the source. We also recycle and reuse materials to minimise the need for waste management or disposal and to conserve resources. We strongly believe that our safety, health and environmental efforts are strong sources of competitive advantage for our business. We have several examples of recycled products actually moving up the value change in our business.

Some of the waste minimisation steps taken by KMML are listed.

Plant	Waste generated	Steps taken	Advantages
1. Ilmenite Beneficiation	Excess Acidic wash water	a) Conservation of water b) Recycling of iron oxide pond water c) Substitution of process water in scrubbers with acidic pond water.	Reduction in HCl consumption
	TiO ₂ fines during leaching	a) Process optimisation b) Use of flocculent	Reduced fines generation.
2. Acid Regeneration Plant	Iron Oxide	a) Lagooned after slurring iron oxide bricks	Production of
	Pond water	b) Recycling back to ARP & IBP	Recovery of chlorides and reduction of HCl demand
3. Chlorination Section	TiCl ₄ vapour Hcl in vent Gases	20% Hcl recovery by enriching in HCl scrubber and recycled back to IBP	Reduction in HCl consumption (20-30%)
	Chlorination waste containing unreacted ore, coke & chlorides of metals.	a) Recover metallic chlorides chloride and regenerate as HCl b) Recover ore & coke.	This will bring effluent level to almost zero.
4. Finishing Section	Excess filtrate water	This water can be utilised for iron oxide washing in ARP	By-product iron oxide washing to remove chlorides.

CONCLUSION

There are three distinct driving forces which are relevant to the near approached century viz; **effect of technology, effect of globalization of business and effect of environmental issues.** The environmental issues are threats and opportunities. The environmental issues are

basically an interaction of forces in a triangle viz; **people who are the spoilers of the environment, people who are the protectors of the environment and people who are effected. People who are issue raisers are in the middle of the triangle.**

The spoilers are presently perceived to be the industry. The protectors of the environment are obviously the people from the Government agencies. The current public' perception around the world and certainly in India is that Industry is a dragon which goes on spoiling everything in its path and it will continue to be the target of attack in India and the rest of the world. However, the biggest spoiler - poverty and population - is escaping the perception of people.

The environmental issues generally come to the fore when there is some amount of pressure. The pressure on industry is the social expectations of the industry. The environmental issues will sharpen pressures on industry for development of technology and manufacturing. The industries should consider that maximum innovations are possible only when there are such pressures. Only if we foresee these pressures and act in time we can save organisation and society and survive in future.

It is inevitable that we will have to move at a relatively faster speed on issues relating to environment.