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Status of waste treatment in titanium mineral industries

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ABSTRACT

The titanium mineral industries encompassing mining, mineral separation and value addition activities generate considerable quantities of wastes primarily in the form of iron chloride/sulphate, iron oxide and acidic effluents. This paper presents a brief review of various value addition activities and associated waste generation issues. Special reference is made of the problems faced by Indian plants engaged in the processing of titanium minerals.

Keywords : Waste treatment, Titanium mineral industries, Effluents, Value additions.

INTRODUCTION

India is endowed with the largest reserves of titaniferrous ores in the world. The resources so far identified are estimated to be 278 million tonnes (mt) in terms of available titanium mainly as minerals like ilmenite and rutile. The world resources of ilmenite and rutile in terms of available titanium is estimated to be 1362 mt. About 2400 km coastal length of Kerala, Tamil Nadu, Andhra Pradesh, Orissa, Karnataka and Maharashtra is enriched in ilmenite, leucoxene, natural rutile alongwith other heavy minerals such as zircon, monazite, sillimanite and garnet. Fig. 1 provides the locations of various deposits. Table 1 compares analyses of various elements present in ilmenite available in major Indian reserves. Indian Rare Earths Ltd (IRE) is presently operating three mineral separation plants one each at Chavara(Kerala), MK (Tamil Nadu), and OSCOM (Orissa) to produce about 3 lakh tonnes of ilmenite,12 thousand tonnes of rutile and other heavy minerals taking advantage of the difference in their specific gravity,magnetic and electrostatic properties. A simplified process flowsheet for the separation of titanium minerals is presented in Fig. 2. It can be seen from this Figure that the mining operation generates a tail which can be considered as mining waste as it contains very small quantities of heavy minerals. Such a tail is however effectively used for backfilling of the mined out site and its restoration. The tails from Concentration Upgradation Plant (CUP) and Mineral Separation Plant (MSP) are stockpiled for its future use depending on its heavy mineral contents.

Table 1 : Analysis of Indian Ilmenite (in wt %)

	TiO_2	Fe_2O_3	FeO	Cr_2O_3	V_2O_5	P_2O_5
Chavara	60.00	25.60	9.23	0.13	0.15	0.20
Manavalakurichi	55.00	18.90	20.90	0.08	0.22	0.12
Nevra (Ratnagiri)	53.25	22.50	23.56	0.07	0.41	0.16
Kudiraimoli	52.63	16.86	29.52	0.001	<0.004	0.29
Kalpakkam	51.00	15.96	30.40	0.06	1.10	0.59
Chatrapur	50.20	12.76	34.19	0.05	0.24	0.03
Santankulam	49.56	14.41	28.08	0.001	<0.004	0.22

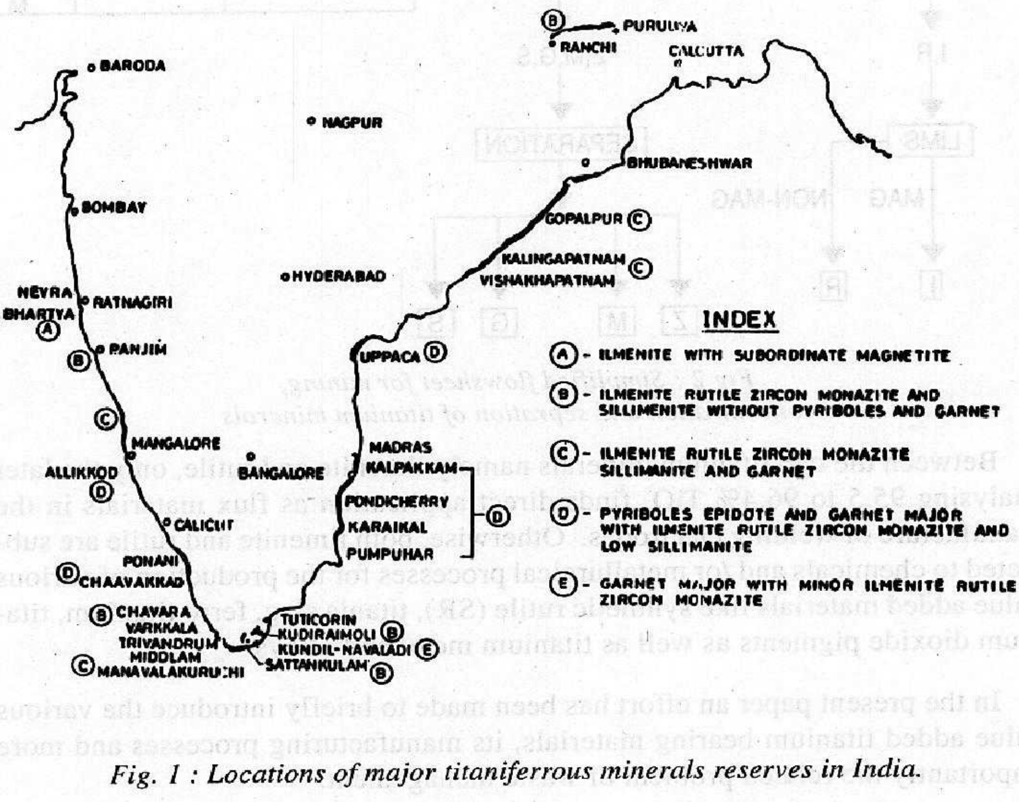
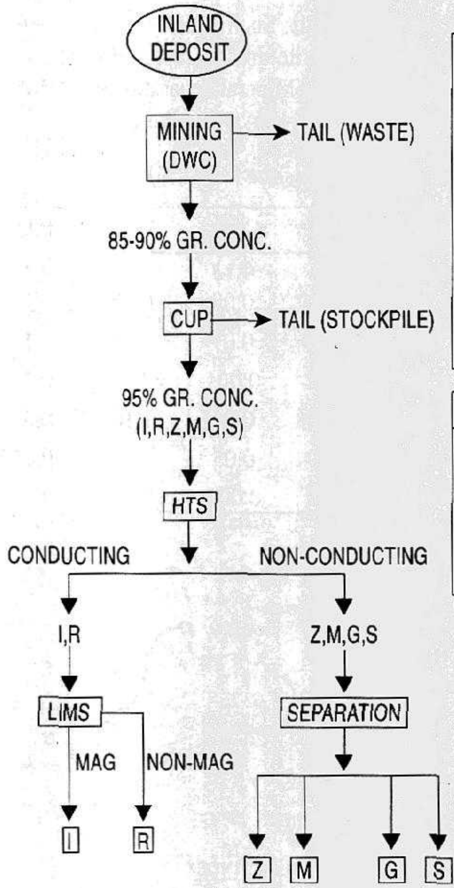


Fig. 1 : Locations of major titaniferrous minerals reserves in India.



I - ILMENITE	M - MONAZITE
R - RUTILE	G - GARNET
Z - ZIRCON	S - SILLIMANITE
CUP - CONC. UPGRADATION PLANT	
HTS - HIGH TENSION SEPRATOR	
LIMS - LOW INTENSITY MAG SEPARATOR	
DWC - DREDGE AND WET CONCENTRATOR	

CONDUCTING	MAGNETIC	SP.GR
I	I	S
R	G	G
	M	R
		I
		Z
		M

Fig 2 : Simplified flowsheet for mining, concentration and sepration of titanium minerals

Between the two titanium minerals namely ilmenite and rutile, only the later analysing 95.5 to 96.4% TiO_2 finds direct application as flux materials in the manufacture of welding electrodes. Otherwise, both ilmenite and rutile are subjected to chemicals and /or metallurgical processes for the production of various value added materials like synthetic rutile (SR), titania slag, ferro titanium, titanium dioxide pigments as well as titanium metal and alloys.

In the present paper an effort has been made to briefly introduce the various value added titanium bearing materials, its manufacturing processes and more importantly the related problem of waste management.

SYNTHETIC RUTILE (SR)

SR analysing 92-97% TiO_2 is the closest substitute for rutile and finds use as feed stock for the manufacture of titanium dioxide pigment. Chemical analysis of a typical SR sample made by IRE, OSCOM, Orissa is presented in Table 2. For upgrading the TiO_2 content of natural ilmenite to form SR, a number of chemical processes (Wah-Chang, Benilite, Musro and Austpac) are avilable. Each of these processes employ various combinations of thermal oxidation to break the ilmenite structure, thermal reduction to convert ferric oxide to easily leachable ferrous oxide, leaching of the reduced ilmenite with hydrochloric acid to remove iron oxide and treatement of the iron chloride bearing spent acid to regenerate and recycle hydrochloric acid. Three Indian Companies namely IRE at Orissa, Kerala Minerals and Metals Ltd. (KMML), Kerala and Cochin Minerals and Rutile Ltd (CMRL), Kerala, are producing SR by using above mentioned technologies. Various industrial wastes and by-products generated by these companies are presented in Table 3. It can be seen from this Table that removal of iron oxide from ilmenite leads to generation of iron chloride bearing acidic solution on account of following reactions :

Table 2 : Analysis of SR made by OSCOM, (IRE) [in wt %]

TiO_2	Fe_2O_3	SiO_2	Al_2O_3	MgO	CaO	MnO	Cr_2O_3	Moist	LOI
91.2	5.0	2.6	0.6	0.08	0.01	0.01	0.04	0.2	0.3

$$Fe_2\,TiO_5\,(Fe_2O_3.TiO_2) + TiO_2 + CO \rightarrow 2Fe\,TiO_3\,(2FeO.TiO_2) + CO_2$$

$$Fe\,TiO_3 + 2\,HCl \rightarrow FeCl_2 + H_2O + TiO_2$$

$$Fe_2\,TiO_5 + 6\,HCl \rightarrow 2FeCl_3 + 3H_2O + TiO_2$$

Generation of huge quantities of acidic iron chloride solution is not only an environmental threat but also requires suitable treatment for improving the process economy. DCW, Tuticorin was continuing the practice of throwing such solution to sea till recently but now planning to set up facility for the recovery of ferrite grade iron oxide after purifying the leach liquor through solvent extraction. CMRL, Cochin, on the other hand has set up a chlorination facility for converting all the ferrous iron present in the spent acid to ferric chloride and exporting the same for sewage treatment.

The Benilite process, as practiced by OSCOM, (IRE) and KMML, on the other hand involves operation of acid regeneration plant to recover HCl as per following reactions :

Table 3 : Synthetic Rutile Plants in India

Company & Installed Cap, (TPA)	Feed Stock	Present Production (TPA)	Process	Waste generated
CMRL, 10,000	Chavara Ilmenite	18,000 95-96% Gr. for export	Wah Chang process Reduction roasting-two stage leaching with 30% HCl	Iron chloride solution
KMML 25,000	-do-	18,000 89% Gr. for inhouse use	Benilite Process Reduction roasting- 2 stg leaching with regenerated acid	Iron oxide and dilute acidic effluent
DCW 20,000	MK ilmenite	18,000 95% Gr. For export	Wah Chang process	Iron chloride solution
OSCOM 100,000	Orissa ilmenite	7000 92% Gr. for export	Benilite process	Iron oxide and dilute acidic effluent

$$FeCl_3 + \frac{3}{2} H_2O \rightarrow \frac{1}{2} Fe_2O_3 + 3\,HCl$$

$$2\,FeCl_2 + 2\,H_2O + \frac{1}{2} O_2 \rightarrow Fe_2O_3 + 4\,HCl$$

Although such a scheme regenerates acid for recycle at much lesser cost than that of fresh acid, it generates considerable quantities of fine sized iron oxide powder (Table 4). Disposal of such material or finding suitable commercial use is indeed a challenge.

The most recent technology on making SR has been introduced by an Australian Company, Austpac Gold. AUSTPAC process carries out the oxidation-reduction of the ilmenite in a specially designed fluidised bed furnace before leaching it with regenerated acid (20%) in a fluidised bed leaching assembly at atmospheric pressure. The spent acid is converted into solid iron chloride pellets before its treatment for acid regeneration. Such a process is claimed to be cheaper than the conventional acid regeneration plant and yields iron oxide in the granular form which is environmentally more acceptable.

Table 4 : Analysis of iron oxide powder generated by Synthetic Rutile Plant, OSCOM, IRE

Chemical Analysis, Dry % wt basis							
Fe_2O_3	TiO_2	MgO	MnO	Al_2O_3	SiO_2	V_2O_5	Cr_2O_3
85-92	1.5-8	1-1.2	0.8-1.4	0.8-1.5	0.5-1.5	0.2-0.3	0.06

Size analysis					
Micron	+80	-80+50	-50+20	-20+01	-01
Wt,%	0.6	9.5	57.4	24.8	7.7

In comparison to the above mentioned reduction roast-acid leaching processes, a more successful and different approach was first developed by R.G. Becher in the Western Australian Government Chemical Laboratories. Subsequently, it was integrated with two existing processes developed by Steel Company of Canada (STELCO); Lurgi GmbH, Germany; Republic Steel Corporation, USA and National Lead Corporation, USA. In the present form it is known as SL/RN Becher process. In this process, the iron oxide in ilmenite is reduced to metallic iron in a rotary kiln by using bituminous coal as a reductant at about 1100°-1200°C. The reduced material is subsequently aerated in 1 to 2% ammonium chloride solution to rust out iron. The rusted iron is then separated by physical means. Any unconverted iron present in the synthetic rutile is removed by dilute acid leaching. The entire reaction of iron removal is carried out at atmospheric pressure and 60° to 70°C temperature. The process consumes much less energy compared to the acid leaching processes described earlier and generate little liquid effluent. However, disposal of huge quantities of very fine iron oxide is again a draw back of this process. The range of iron oxide particles is of the order of 10 to 45 μm and they pose serious environmental problems for disposal in the open. They need careful storage in big lagoons or ponds.

TITANIFERROUS SLAG

In this approach, the problem of generation of iron oxide powder is addressed by carbothermic smelting of low grade ilmenite with higher iron oxide contents in electric or plasma furnace to produce titaniferrous slag (Table 5) and pig iron

Table 5 : Analysis of typical titaniferrous slag, wt %

TiO_2	FeO	Fe_2O_3	MnO	Cr_2O_3	CaO	MgO	Al_2O_3	SiO_2	U&Th
85.5	10.8	0	1.7	0.17	0.17	1.1	1.3	2.1	30ppm

Table 6 : Metallurgical process options for beneficiation of ilmenite to titania slag

Process	Description	Plant Status
QIT Electrosmelting	C- smelting of hard rock ilmenite at 1700°C to pig iron(PI) and titania slag (86-87% TiO_2)	Sorel, Quebec 1,000,000 tpa slag
RTZ *Iron & Titanium* Electrosmelting	*Same process customised* to suit beach sand ilmenite	Richards Bay, *South Africa* 1,000,000 tpa slag & 5,000,000 tpa PI
Submerged Arc smelting process	Pre-reduction of ilmenite followed by smelting in Arc Furnace to produce PI & Titania slag (87%)	TINFOS, Norway 200,000 tpa slag + 100,000 tpa PI
Plasma DC Arc smelting technology (South Africa Anglo American Corp.)	C- smelting of ilmenite in DC Arc Plasma furnace to PI and slag	Namakwa Sands Ltd, SA, 100,000 tpa slag & 45,000 tpa PI ISCOR, SA, 220,000 tpa slag from 1999
Upgraded Slag Technology, QIT	Conditioning of the Sorel Slag, its acid leaching and calcination to 95% TiO_2	Sorel, Quebec, 200,000 tpa of slag to be expanded to 600,000 tpa

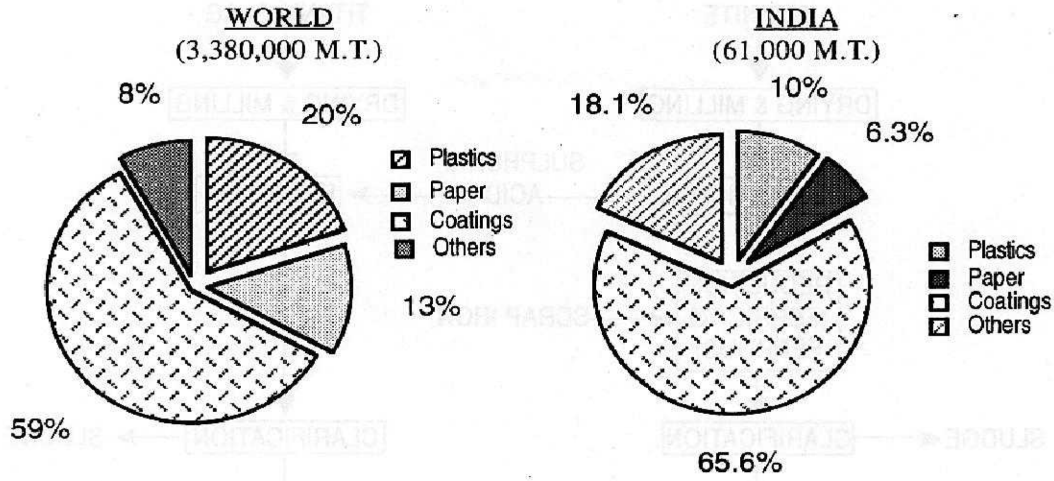
which is a saleable product. Table 6 presents the details of various overseas companies practicing such scheme. It may be noted that no Indian Company is yet to examine this energy intensive process on account of higher power cost in our country.

FERROTITANIUM

Ilmenite analysing 60% TiO_2 can be converted to low carbon ferro titanium analysing 27-28% Ti, 8% Al (max) and 3% Si by aluminothermic reduction according to the following reaction :

$$FeO.\ TiO_2 + 2Al \rightarrow Fe\ Ti + Al_2O_3$$

The reaction can be carried out in refractory lined open top rectangular or cylindrical reactor in the presence of $KClO_3$ as energy booster and lime as a flux



Others inlcude : Catalysts, Ceramics, Cosmetics, Electronics, Fibreglass, Flooring, Food, Leather, Pharmaceuticals, Printing inks, Roofing, Rubber, Textiles and Titanium compounds.

Fig. 3 : Utilisation pattern of TiO_2 in the world and India.

to achieve alloy yield of about 60%. Here again, the calcium aluminate slag carrying unreduced ilmenite and silica is considered to be a waste material. It can, however, be partly put in use by crushing to powder form for use as lining materials for the reactor.

TITANIUM DIOXIDE PIGMENT

The principal use of titanium minerals is for manufacture of titanium dioxide pigment which is extensively used in plastics, paper, paint and other industries such as leather, ceramics, rubber, pharmaceuticals, chemicals, textiles, foods, electronics, printing ink etc. Fig. 3 represents the global share of above industries in utilising titanium dioxide. The pattern of consumption of TiO_2 in India is also presented for comparison. As against world consumption of 3.38 mt of TiO_2, the Indian demand was only a miniscule of 0.061 mt. Indigenous manufacture of TiO_2 catered to only 52.5% of above consumption and the balance quanatity was supplied through import. Fig. 4 shows the world wide scenario of installed capacity for production of titanium dioxide during last 50 years. Titanium dioxide for its use as a pigment is 99.9% pure TiO_2 falls into two categories viz. Rutile and Anatase grades. Both these grades are essentially pure TiO_2 having different crystal structures. These titanium dioxide materials can be produced either by the sulphate or chloride route.

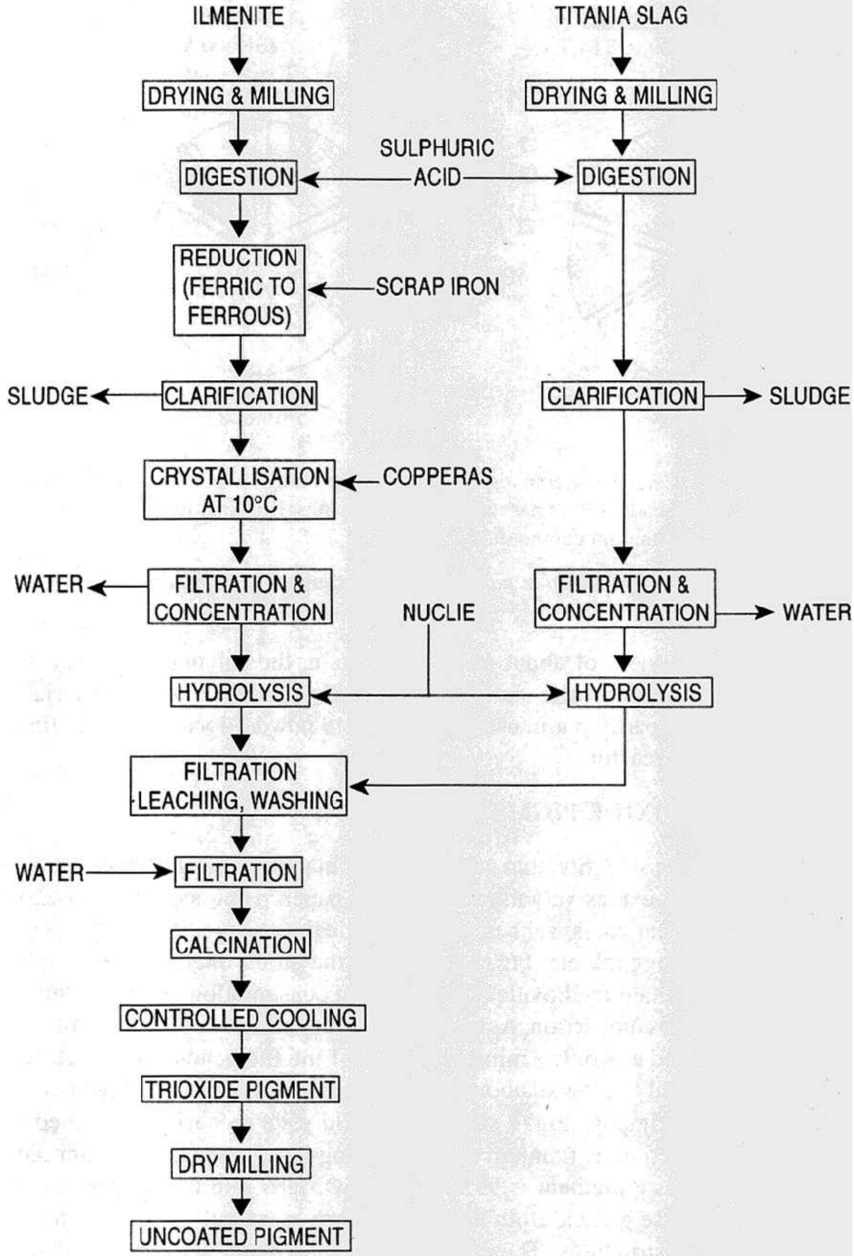


Fig. 4 : Flow sheet for the production of TiO_2 by sulphate route.

The sulphate route involves digestion of ilmenite with concentrated sulphuric acid to form soluble titanium oxysulphate and iron sulphate. After the separation of iron sulphate by crystallisation, the titanium oxysulphate is subjected to hydrolysis. The hydrolysed titanium is dried and calcined to yield titanium dioxide of anatase or rutile grade depending upon the calcination temperature. The essential chemical reactions involved in the process are presented below:

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

$$TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4$$

$$Ti(OH)_2 \rightarrow TiO_2 + H_2O$$

The process flow sheet for the sulphate route is presented in Fig. 4. It can be seen that iron sulphate known as copperas as well as dilute sulphuric acid are generated during the manufacturing process requiring their safe disposal as waste materials. Recent developments in process technologies are arising towards concentration of dilute acidic waste for reuse and pyrolytic dissociation of ferrous sulphate for regeneration of acid value. Some attempts have also been reported for producing phosphatic fertilizer from the acidic waste.

The chloride route on the other hand involves anhydrous chlorination of rutile or SR in the presence of carbon to form $TiCl_4$, its purification and high temperature oxidation followed by controlled cooling to yield rutile grade titanium dioxide and chlorine for recycle as per the following reactions:

$$2TiO_2 + 3C + 4Cl_2 \rightarrow 2TiCl_4 + CO_2 + 2CO$$

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

The flow sheet for the chloride route is presented in Fig. 5. Depending upon the composition of the feed stock this process will also yield iron chloride as a solid waste which is required to be disposed off safely or put into some use. It should also be noted that quality of pigment depends on the presence of impurities in $TiCl_4$. Hence $TiCl_4$ is purified by adoption of various chemicals which form easily separable complexes with the impurities. The impurities like Ca, Mg, Cr and Mn form high boiling chlorides during fluid bed chlorination and can be separated from $TiCl_4$ by condensation of chlorinated vapour. Both low volatility as well as low melting points of calcium and magnesium chlorides generated by Ca and Mg content of synthetic slag or upgraded ilmenite create difficulties in the stability of the fluidised bed by agglomerating particles. The arsenic, antimony, vanadium, silica and iron chlorides are low boiling and highly volatile in nature. They condense along with $TiCl_4$. Chlorides of vanadium and

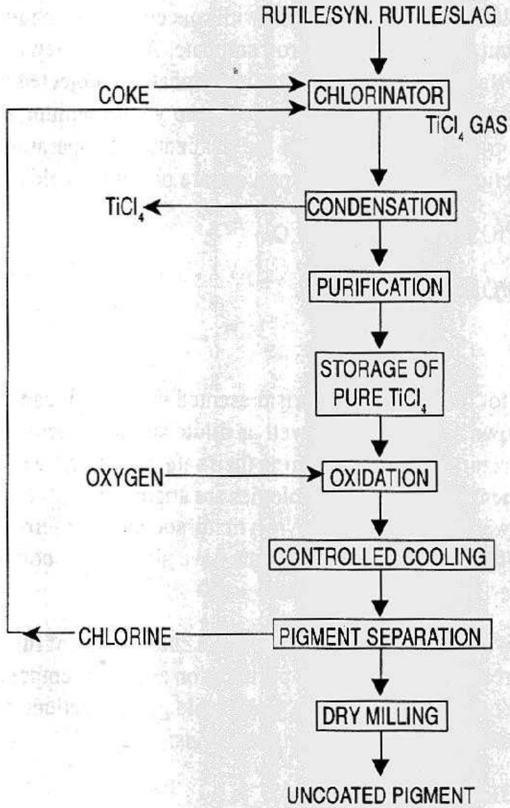


Fig. 5 : Flow sheet for the production of TiO_2 by chloride route.

iron are removed by simple selective condensation/reduction procedure which is sufficient for pigment production. It is reported that every one percent increase in the value of iron oxide concentration in the feed stock enhances the cost of TiO_2 manufacture by 3%. The chromium, vanadium and niobium contents in the feed stock adversely affect the brightness of the pigment and consequently lower the hiding power of the pigment during processing. The presence of silica above 1% in the ore or chlorinatable beneficiated ore is not desirable as high silica in the feed results in difficulties in purifying $TiCl_4$. Increased environmental awareness in the developed countries, who are also the major consumers and producers of TiO_2 have severely restricted the upper permissible limit of radioactive nuclides concentration in the chlorinatable feed stock to only 80 ppm. Table 7 gives the upper acceptable limits of various impurities in the chlorinatable feed stock. A feed stock low in impurities and high in titanium value results in improved overall plant performance due to higher yield of product, lower cost of waste management and lower inputs of chemical reagents.

Table 7 : Chloride feed stock specification

Al_2O_3	SiO_2 & ZrO_2	CaO	MgO	MnO	U & Th	Particle Size
2% max	2% max	0.2% max	1% max	2% max	80 ppm max	>100 micron

It can be seen from Fig. 6 that the chloride route has been taking precedence over the traditional sulphate route since its inception in 1965. Capacity addition for sulphate route based process have been only marginal during the past decade compared to growth in chloride route based plants. Preference for chloride route process to that of sulphate route is mainly due to 50% saving in energy consumption and reduction in effluent generation by 80%. Table 8 shows the typical values of pollutants generated by both the processes for comparison. In India, only M/s. KMML has an installed plant capacity of 22,500 tpa rutile grade pigment based on chloride route. The other three pigment manufacturers i.e., M/s. Travancore Titanium Products, Trivandrum, M/s. Kilburn Chemicals, Tuticorin and M/s. Kolmac Chemicals, Calcutta have processes all based on sulphate route and have installed capacities of 24,500 TPA, 3960 TPA and 2400 TPA

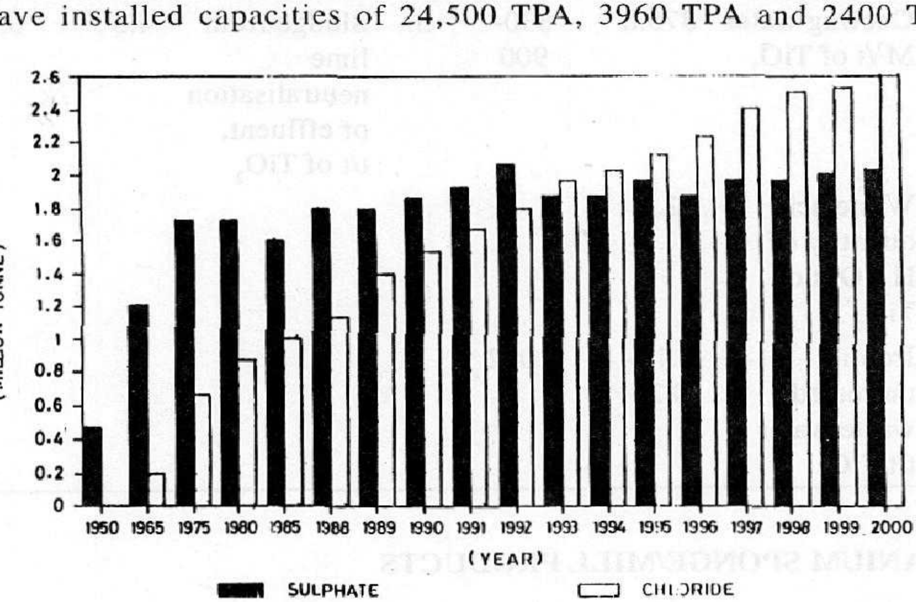


Fig. 6 : World TiO_2 production capacity yearwise comparison of sulphate v/s. chloride routes.

respectively. All of them face ferrous sulphate and acidic effluent disposal problems. Though chloride route plants are preferred world over for their energy economy and potential for environment friendly waste production, the technology is a closely guarded secret by a few multinationals such as DuPont and Kerr McGee. The classical sulphate route plants are easier to build as the materials of construction and equipment are available in a developing country like India. Table 9 gives a comparative advantage and disadvantage of both the processes.

Table 8 : Typical Pollutants generated by sulphate and chloride plants

Sl. No.	Item	Sulphate	Chloride	Sl. No.	Item	Sulphate	Chloride
	Liq. waste				Solid waste		
1.	Waste acid streams M^3/t of TiO_2	65.0	-	1.	$FeSO_4$ t/t of ilmenite	2.4	-
2.	Other process streams M^3/t of TiO_2	41.7	32	2.	Ore residue t/t of TiO_2	0.13-6.2	Negligible
3.	Cooling water M^3/t of TiO_2	375.0	630-900	3.	Sludge from lime neutralisation of effluent, t/t of TiO_2	4.5	0.07
4.	Waste acid quantity of H_2SO_4/t of TiO_2	2.4	-				
5.	Iron in untreated waste water t/t TiO_2	0.16-0.26	0.002				

TITANIUM SPONGE/MILL PRODUCTS

Another step in value addition on titanium minerals is production of titanium sponge and mill products. Starting with the purified $TiCl_4$ generated by chlorination of feed stock like synthetic rutile or rutile, as in the case of chlo-

Table 9 : Comparison of sulphate and chloride routes for TiO_2 production

Sl. No.	Description	Chloride route	Sulphate route
1.	Raw material	Rutile, beneficiated ilmenite/lecoxene mixture	Ilmenite, Titania slag
2.	Process	Modern dry process in volves high temperature oxidation of $TiCl_4$	Modernised, wet process involves precipitation and calcination of TiO_2 of acid soluble titania
3.	Product	Rutile grade oxide	Both rutile and anatase grade oxides
4.	Effluent / by-product	Negligible effluent, some $FeCl_3$ is generated and chlorine is recycled	Small to large quantity of iron sulphate and spent acid are generated
5.	Hazards	Handling of $TiCl_4$ and chlorine	Handling of concentrated H_2SO_4
6.	Plant costs & energy inputs	Plant costs are higher but energy and operating costs are lower.[1.8kWH/kg of oxide]	Energy and operating costs are higher. [2.5kWH/kg oxide but plant cost can be lower]
7.	Other services	O_2 for oxidation of $TiCl_4$, N_2 as protective gas and cooling water	Iron scrap to reduce $Fe_2(SO_4)_3$, large quantity of process and cooling water

ride route for pigment making , commercial production method for titanium sponge involves magnesiothermic reduction (Kroll Process) as shown below :

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

It can be seen from the above reaction that magnesium chloride is a by-product and after its separation from the reduced sponge by vacuum casting and distillation, it should not be disposed as a waste. It should rather be subjected to molten salt electrolysis to recover magnesium as a reducing agent and chlorine for its use in the chlorination of feed stock.

During the subsequent processing of titanium sponge by vacuum arc melting, casting and shaping by mechanical metallurgical processes, considerable quantities of metal scrap is generated. These metal scraps can be proved to be hazardous material taking into account pyrophoric nature of reactive metal like titanium and their gainful utilisation by suitable recycling is called for.

In our country Defence Metallurgical Research Laboratory (DMRL),Hyderabad has established and demonstrated production of 4 T per batch of titanium sponge using combined magnesiothermic reduction - tapping of $MgCl_2$ and vacuum distillation technique and fused salt electrolysis of the byproduct $MgCl_2$ in a 7 KA bipolar cell to regenerate the reducing agent. Based on this technology Department of Atomic Energy (DAE) is proposing to set up a 400 TPA titanium sponge plant at Palaykayal in Tamil Nadu. As per as capability of converting the titanium sponge to various mill products are concerned Mishra Dhatu Nigam (MIDHANI), Hyderabad has 150 TPA plant for the production of hot/cold rolled sheets/plates/bars,wires and welded tubes.

CONCLUSION

Ilmenite is the most abundant and cheapest mineral available for the metal titanium. Since such a mineral is associated with large concentration of iron oxide, any immediate value addition in the form of synthetic rutile by chemical process calls for removal of iron value and thus generation of huge quantities of iron bearing salt as waste. Metallurgical process like carbothermic smelting is a possible solution to such a waste generation problem as it converts iron value to saleable pig iron. Further value addition on various feed stocks to pigment grade titanium dioxide again leads to generation of iron bearing solids and acidic liquid effluents. Recovery of acid value from such effluents and conversion of iron bearing waste to useful material is the only solution to the environmental threat posed by titanium mineral industry.