EXHIBIT J

EUROPEAN COMMISSION

Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques for the Manufacture of

Large Volume Inorganic Chemicals – Solids and Others industry

August 2007

3 TITANIUM DIOXIDE

3.1 General information

3.1.1 Introduction

Titanium dioxide (TiO_2) white inorganic pigments are used primarily in the production of paints, printing inks, paper and plastic products. TiO_2 is also used in many white or coloured products including foods, cosmetics, UV skin protection products, ceramics, fibres, rubber products and more. Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties, its chemical stability, and lack of toxicity [13, EIPPCB, 2000]. Titanium dioxide pigments are made from one of two chemical processes: the chloride route, which leads to TiO_2 products by reacting titanium ores with chlorine gas; and the sulphate route, which leads to TiO_2 products by reacting titanium ores with sulphuric acid. Chloride and sulphate pigments are both used in a wide range of applications. There are some preferred end uses for pigments from each process.

As illustrated in Table 3.1, in 1996 world TiO_2 consumption reached nearly 3.4 million tonnes; approximately 59 % go into paints, 20 % into plastics, and 13 % into paper.

Use	Consumption, kt	Percentage (%)
Coatings	1988	59
Paper	424	13
Plastics	686	20
Others	286	8
Total	3384	100

Table 3.1: World consumption of TiO_2 pigments in 1996
[87, Ullmann's, 2001]

Estimated 1993 – 2000 growth rates of TiO_2 consumption by region, given in Table 3.2, illustrate that the titanium dioxide industry is one of the most dynamically developing segments of the global chemical industry sector.

End use	US	Middle & Eastern Europe, Africa	Asia and Pacific	World total
Coatings	3.4	2.0	5.0	2.5
Paper	2.0	4.0	4.0	3.0
Plastics	4.5	5.0	10.0	5.5
Total	3.0	2.5	6.5	3.3

Table 3.2: Annual growth rates of TiO_2 use (1993 – 2000, %)
[87, Ullmann's, 2001]

Titanium dioxide is the most important inorganic pigment in terms of quantity. The world production in 2000, amounting to nearly 4 million tonnes per year, is given below in Table 3.3:

Year	Sulphate process $^{(2)}$		Chloride process		Total
	kt per year	%	kt per year	%	kt per year
1965	1254	90.3	135	9.7	1389
1970	1499	77.4	437	22.6	1936
1977	1873	72.3	716	27.7	2589
1988	1781	60.2	1178	39.8	2959
1995	1481	46.0	1739	54.0	3220
2000 $^{(1)}$	1540	40.0	2310	60.0	3850
(1) Estimated; (2) A number of plants based on the sulphate process have recently been commissioned in China.					

Table 3.3: World production of TiO_2 pigment
[87, Ullmann's, 2001], [85, EIPPCB, 2004-2005]

World TiO_2 pigment production capacities in 1995 by region are given in Table 3.4.

Country	Capacity, kt per year		
	Chloride	Sulphate	Total
Total America	1381	211	1592
Total W. Europe	364	930	1294
Total E. Europe	0	216	216
Total Africa	0	38	38
Total Australia	143	35	178
Total Japan	55	289	344
Total Far East	137	109	246
Total world	**2080**	**1828**	**3908**

Table 3.4: World TiO_2 pigment production capacities in 1995 by region
Based on [87, Ullmann's, 2001]

World TiO_2 production capacities in 1995 were split approximately to 47 % for the sulphate process and 53 % for the chloride process.

Present capacities of the EU-25 (plus Norway) titanium dioxide industry and TiO_2 producers, illustrated by country, company, location and the capacity in either the chloride or sulphate process route, are given in Table 3.5.

Country	Location	Capacity, kt per year		
		Chloride	Sulphate	Total
Germany	Leverkusen	100	30	130
	Nordenham		62	62
	Krefeld-Uerdingen		130	130
	Duisburg-Homberg		100	100
UK	Grimsby		80	80
	Greatham	100		100
	Stallingborough	150		150
France	Le Havre		95	95
	Thann		30	30
	Calais		100	100
Finland	Pori		120	120
Italy	Scarlino		80	80
Belgium	Langebrugge	60		60
Spain	Huelva		80	80
Netherlands	Rotterdam	55		55
Norway	Fredrikstad		30	30
Czech Republic	Prerov		41	41
Poland	Police		40	40
Slovenia	Celje		44	44
Total EU-25 + Norway		**465**	**1062**	**1527**
Note: Czech Republic, Poland and Slovenia – updated TiO_2 capacities.				

Table 3.5: EU-25 (plus Norway) TiO_2 pigment production capacities in 2002
Based on [20, CEFIC-TDMA, 2004], [85, EIPPCB, 2004-2005]

3.1.2 General description of the European titanium dioxide industry

The titanium dioxide industry has developed dynamically over the past few decades. From its first commercialisation in the 1920s, the titanium dioxide (TiO_2) product has ever increasingly been used to enhance the opacity, whiteness and brightness of many everyday articles. It is a global industry in which about 1.5 million tonnes of titanium dioxide per year is produced at the 19 European sites. Approximately 30 % of this is produced at five sites by the chloride process. The remainder is made by the sulphate process.

Almost all titanium dioxide is sold as a pigmentary powder to industrial manufacturers of paints, plastics, paper, fibres, printing inks, ceramics and similar products where its purpose is to provide a white or pastel colour.

Over the past 20 years, the European TiO_2 industry has invested as much as EUR 1400 million in environmental improvement [20, CEFIC-TDMA, 2004]. This expenditure was initiated in the 1970s and boosted as a result of the three specific TiO_2 Harmonisation Directives: 78/176/EEC; 82/883/EEC and 92/112/EEC [21, The Council of the EU, 1992], which prescribe minimum environmental performance standards for the titanium dioxide industry, to which the TiO_2 industry is required to comply. Most of this investment has been put into the sulphate process and it is believed that environmentally there is little difference between a modern sulphate process and a modern chloride process [20, CEFIC-TDMA, 2004]. This is discussed further in the subsequent sections. Company environmental cultures have also evolved over the same period, which has resulted in a proactive approach to environmental issues. This has resulted in each company applying environmental techniques most applicable to the process used at their specific sites.

3.1.3 History of markets

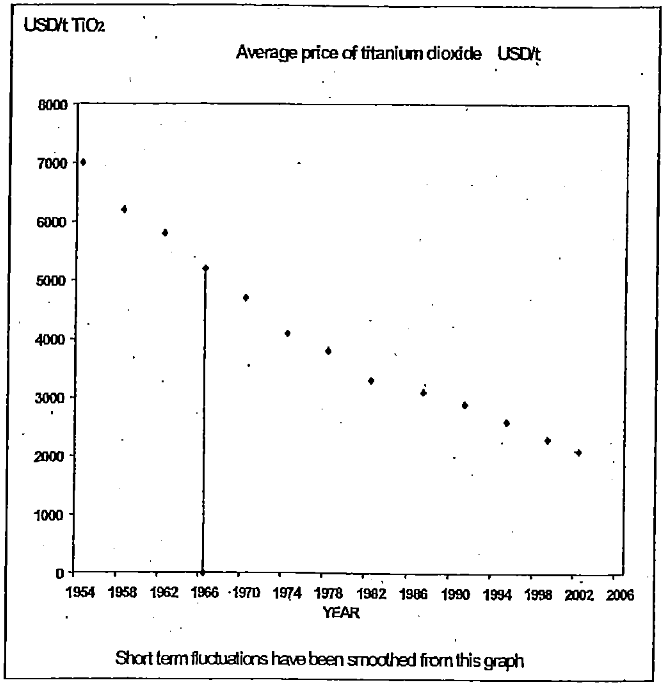
Titanium dioxide pigments have been produced since the end of the First World War, but it was not until the late 1920s that production of high purity anatase pigments by the sulphate process reached commercial levels. These pigments rapidly began to replace the existing pigments such as 'lead white', which itself is toxic. Rutile pigments began to be marketed in the 1940s. Anatase and rutile are different crystal forms of TiO_2; rutile makes a generally superior pigment but is not suitable for all applications.

Commercial chloride pigment production was introduced in the late 1950s. World sales of TiO_2 pigments grew to 1 million tonnes per year by 1963, achieved over 2 million tonnes by 1977 and reached over 3.9 million tonnes by the end of the 1990s. Once it was established, the overall TiO_2 market grew broadly in line with world Gross Domestic Product (GDP).

The long term growth rate for the titanium dioxide industry is just under 3 % per year. For most of the 1990s, the titanium dioxide industry in Asia had been growing significantly faster than the worldwide long term rate and today represents 20 % of the world market, with north America at 38 % and Europe at 30 %. The global production capacity is approximately 55 % chloride and 45 % sulphate compared with 30 % chloride and 70 % sulphate in Europe. No new plants have been built in Europe for more than a decade. Some markets require pigment specifically from either the chloride process or the sulphate process, but for around 80 % of end-use, pigments from either process can be produced to meet the customer's needs equally well.

The whiteness and brightness of the TiO_2 pigment requires that the base material is made to a high degree of purity and its suitability for different uses is dictated by its particle size and final treatment (coating).

As illustrated in Figure 3.1, there has been a downward trend in prices in real terms over the past three decades in all regions, and it is clearly visible when average TiO_2 prices are analysed over that period. This has resulted in considerable efforts to improve plant efficiencies and increase the scale of operations in order to reduce costs.



Short term fluctuations have been smoothed from this graph

Figure 3.1: Trend prices in titanium dioxide pigment commodity product
[20, CEFIC-TDMA, 2004]

There is a significant fluctuation in the long term trend price in all regions, depending on changes in the supply and demand balance within each region. The variable and cyclic nature of demand means that it is very difficult to plan plant capacity increases in time correctly, and historically it has been seen that new capacity is often just coming on stream as the market begins to turn down. It should be noted that the cycles in the titanium dioxide industry are not expected to always be in phase with the overall chemicals industry cycle.

3.1.4 Producer companies

Five companies account for about 80 % of the global market. Throughout much of the 1990s there has been an excess capacity in the industry and intense competition amongst producers.

These market conditions have tended to favour the larger and more cost competitive producers. In addition, prices have not been at levels sufficient to justify major new investments in production capacity. All these factors have led to some consolidation in the industry recently [20, CEFIC-TDMA, 2004], [8, CEFIC, 2004].

European plants covered by this document are situated in the UK, Germany, France, Italy, the Netherlands, Belgium, Spain, Finland, Czech Republic, Poland, Slovenia, and Norway – see Table 3.5 and Table 3.6. However, apart from the Czech Republic, less information is available for the other new Member States.

The majority of the plants were built during the period 1948 to 1980, but they have all undergone major overhauls during the last 12 years and some have been shut down and replaced with a new plant on the same site.

Table 3.6 illustrates a very high cost burden for the European TiO_2 industry, in particular in older plants based on the sulphate route, to cope with more and more stringent emissions levels. Because of the economic situation in the industry, new grass root plants are unlikely to be built but the trend is to debottleneck or build new streams on existing locations. On average, environmental improvement has increased running costs by 10 to 15 %.

Company	Location	Process route	Environ-mental Capex EUR million	Capex period	Factory start-up year
Company A	Fredrikstad, Norway	Sulphate	20	1988 to 1999	1916
	Langerbrugge, Belgium	Chloride(1)	75	1987 to 1999	1957 (SP) 1989(CP)
	Nordenham, Germany	Sulphate	70	1986 to 1999	1969
	Leverkusen, Germany	Chloride and Sulphate	125	1982 to 1999	1972 1927
Company B	Grimsby, UK	Sulphate	59	1990 to 1999	1948
	Greatham, UK	Chloride	19	1990 to 1999	1971
	Huelva, Spain	Sulphate	67	1990 to 1999	1973
	Calais, France	Sulphate	146	1990 to 1999	1967
	Scarlino, Italy	Sulphate	40	1985 to 1999	1974
Company C	Pori, Finland	Sulphate	96	1980 to 1999	1961
Company D(2)	Rotterdam, the Netherlands	Chloride	160	1989 to 1999	1961(3)
	Uerdingen, Germany	Sulphate	34 200	1992 to 2000 up to 1991	1957
Company E	Stallingborough, UK	Chloride	61(4)	1987 to 2000	1968
	Le Havre, France	Sulphate			
	Thann, France	Sulphate	33	1989 to 2001	1922
Company F	Prerov, Czech Republic	Sulphate	15	1990 to 1999	1968
Company G	Duisburg, Germany	Sulphate	125	1987 to 1994	1962
Company H	Police, Poland(5)	Sulphate	11	1995 to 2003	1977
Company I	Celje, Slovenia(6)	Sulphate	?	?	?

(1) The Langerbrugge sulphate plant in Belgium was closed in 1989 and a chloride plant started up in 1989 on the same site.
(2) The Antwerp plant in Belgium was shut down in 2001 due to being too small a unit to run economically.
(3) The Rotterdam sulphate plant in the Netherlands was closed and a chloride plant started up in 1990.
(4) Including EUR 4.8 million on Stallingborough sulphate plant which was closed in 1996.
(5) Data on the Polish plant are based on new information submitted.
(6) The data which also need to be included in the EU-25 scale are those on the TiO_2 plant in Celje, Slovenia.

Table 3.6: TiO_2 industry site details including capital costs of environmental improvements [20, CEFIC-TDMA, 2004], [85, EIPPCB, 2004-2005]

It should be said that over the last decade or so there have been very positive changes in environmental culture of the EU-25 companies producing TiO_2. The attitudes have changed from defensive to proactive. This is demonstrated by the following:

- in the EU-15 all companies listed in this document are signatories to 'Responsible Care'
- six of the 19 sites have achieved ISO 14001 or EMAS and are, therefore, committed to a programme of continual environmental improvement
- seven are actively working to achieve these management standards
- 12 plants issue publicly available annual environmental reports.

These factors have lead to the companies progressively upgrading the equipment and improving management of their plants.

There are in total 19 production sites and 20 TiO_2 plants in the EU-25, as given in Table 3.5. The size of the plants varies from 30 kt up to 150 kt per year (refer to Section 1.1.5.2). About 7000 persons are employed directly in the manufacturing of TiO_2 across Europe [20, CEFIC-TDMA, 2004], [8, CEFIC, 2004].

3.2 Titanium dioxide – the chloride process

3.2.1 Introduction

Titanium dioxide can be made by one of two basic routes: The chloride process covered in Section 3.2, and the sulphate process covered in Section 3.3. In both processes pure titanium dioxide powder is extracted from its mineral feedstock after which it is milled and treated to produce a range of products designed to be suitable for efficient incorporation into different substrates as described above. Although current versions of the two processes have been demonstrated to be environmentally equivalent by the use of life cycle assessment techniques [20, CEFIC-TDMA, 2004] (see Section 3.4.5), the two processes are fundamentally different in most aspects. Therefore, in this document the processes and their emission abatement techniques are treated separately. A comparison of the two processes is included in Section 3.4.

3.2.2 Applied processes and techniques – the chloride process

As illustrated in Figure 3.2, chlorine gas is used as an intermediary in the process and is recovered for re-use. The chloride process can treat a wide range of ores including natural rutile (95 % TiO_2), titanium rich slag and synthetic rutile (90 – 93 % TiO_2). Higher concentration ores are preferred to minimise chlorine losses, because impurities, such as iron in the ore feed result in a net loss of chlorine. Significant quantities of make-up chlorine gas are required for low TiO_2 content feedstocks.

3.2.2.1 Raw material import and preparation

Ore containing titanium dioxide is sourced from outside Europe. In the past, it was normally high grade mineral rutile, however in recent years this has become increasingly scarce and costly and has been replaced by a material whose TiO_2 content has been artificially upgraded. This can be a slag from a blast furnace process in which the iron is extracted for use in its own right or a synthetic rutile in which metals (mainly iron) are leached out with dilute acid. This is typically done at the quarrying site of the primary ore. The environmental impact of these beneficiation processes is taken into account when making a comprehensive environmental comparison of the chloride process with the alternative sulphate process.

In a life cycle assessment used to compare the two processes (see Section 3.4.5), both the energy use and associated emissions resulting from the TiO_2 beneficiation process are taken into account, to analyse the overall environmental burden for modern TiO_2 manufacturing processes.

Suppliers of ore upgraded by wet methods should be encouraged to use environmentally acceptable methods of leaching the original feedstock and disposing of the wastes. There is potential here for developing co-products from the waste streams. It is a core principle of ISO14001 to require suppliers and customers to commit to environmental improvements and this is a clear example.

Similarly, slag producers should be encouraged to have an active environmental policy and procedures for producing the slag.

The wet mineral feedstock may be stored in stockpiles without problems but before feeding it to the titanium dioxide plant the ore has to be dry. Usually feedstock drying is not necessary, but in the event of the moisture specification being exceeded, drying is usually done in flue-gas dryers heated directly at about 120 °C. Currently feedstock drying is not carried out in any of the European sites, except for one site where ore and coke material from chlorinator blow-over is recovered in a wet state and must be dried before re-use. The dry dust is separated from the flue-gas by cyclones and filters and fed to the chlorinators.

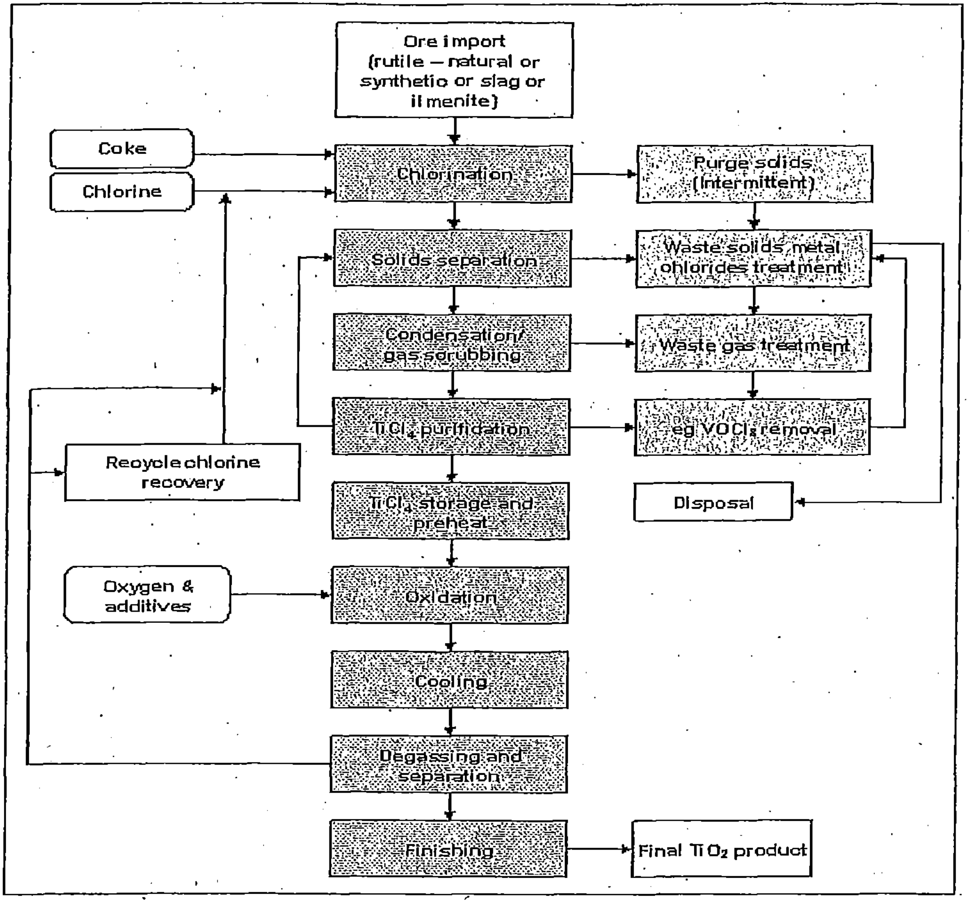


Figure 3.2: Outline flow diagram – TiO_2 chloride process route
[20, CEFIC-TDMA, 2004]

Feedstock purchasing decisions are multidimensional (economic, plant operability, product quality, cost of abatement, waste disposal, etc.) and can change over time. The feedstock of the required purity is purchased according to a set of specifications, set as part of the feedstock purchasing strategy. One of the critical factors is the question of impurities and, therefore, the purity check of titanium ore plays an important role in the production process.

There are two main issues here. Some heavy metal impurities are not acceptable since trace levels in the final product can influence the whiteness and brightness. The other issue is trace levels of Naturally Occurring Radioactive Materials (NORM) which are present in some ores. This means that with these feedstocks the processing is subject to the Euratom Directive, 96/29 [22, Euratom, 1996], which may mean that the ore handling and disposal of some wastes is subject to exposure assessment.

The companies take all necessary precautions to protect personnel and the environment as required by Euratom.

The other main solid raw material is coke, which is required in a granular form suitable for fluidisation in the chlorination process.

If drying is required, it results in normal furnace gaseous emissions (NO_X, SO_X, etc.), however the main issue in feedstock preparation on site is dust emissions during the movement of materials. Normally this is controlled by handling the ore in closed systems kept under reduced pressure with the dust being collected in cyclones and filters for re-use.

Table 3.7 illustrates components in the main mineral feedstocks for the titanium dioxide industry based on the chloride process route.

Type of feedstock	Component	Portion (mass content in %)
Mineral rutile	TiO_2	95 – 96
Slag	TiO_2	86 – 87
Synthetic rutile	TiO_2	90 – 93

Table 3.7: Components in the main mineral feedstocks for the titanium dioxide industry [20, CEFIC-TDMA, 2004]

Another main raw material involved at this stage is chlorine, which is invariably recycled within the process, with any 'make up' chlorine usually being imported by tanker as a liquid. The hazardous nature of chlorine is the main property, which influences the basic design of the chloride process. This means that the initial primary stages of the process (the 'black end') are totally enclosed and of high integrity. In Europe, all processes are controlled by the Seveso II EU Directive regulations [23, The Council of the EU, 1996] and by the Titanium Dioxide Harmonisation Directive [21, The Council of the EU, 1992], which require detailed hazard assessments to be carried out and minimal emissions of chlorine into the environment respectively. Chlorine is delivered by pipeline rail and road depending on the site location.

Pure gaseous oxygen is essential to ensure full oxidation of the titanium tetrachloride. This is normally obtained off-site by pipeline, however, it can be cost effective to have the liquefaction plant close to the TiO_2 site. Increasingly, nitrogen gas (which is obtained from the same source) is used as a gland purge gas to minimise moisture ingress.

3.2.2.2 Chlorination

Ore containing titanium dioxide and coke are fed to a fluidised-bed reactor where an exothermic reaction with chlorine gas takes place at 1000 °C. The primary reaction is:

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

Impurities such as iron oxide will react in a similar manner:

$$FeO + Cl_2 + C \rightarrow FeCl_2 + CO$$

Impurities such as silica and zirconium do not chlorinate and may accumulate in the reactor. There is, however, a natural attrition and carryover of fines along with the off-gases, and this may be sufficient to prevent their build-up. Otherwise the solids will require periodic removal. The reactors may require total bed replacement about once a year.

In one location, coke and unreacted bed material is separated and re used as raw material feed.

3.2.2.3 Solids separation

The resulting vapours of titanium tetrachloride plus other volatile metallic chloride impurities are cooled with recycled cold $TiCl_4$, which allows the removal of some impurities.

3.2.2.4 Waste solid metal chlorides treatment

Solid metal chlorides are usually neutralised with lime which renders the residual metals insoluble before disposal as a solid waste to landfill. Historically, many attempts have been made to treat the metal chlorides to recover the chlorine. This has usually been done with the objective of using feedstocks with a lower TiO_2 content such as ilmenite. This development has never been commercially successful. At one site, ore and coke are separated from the metal chloride stream prior to this stage and filtered and stockpiled for re-use as a feedstock. At another site, separated coke is sold commercially, and the same site markets ferrous chloride ($FeCl_2$).

3.2.2.5 Condensation

The majority of the titanium tetrachloride is condensed from the gas stream and pumped to a dedicated storage facility. More impurities and tetrachloride are removed from the gas stream by jet scrubbing with cold tetrachloride, which is also pumped to storage. The gas stream is then passed for waste gas treatment.

3.2.2.6 Waste gas treatment

See Section 3.2.2.14 below – Abatement systems for gases.

3.2.2.7 Distillation

Further purification of $TiCl_4$ by distillation is carried out and the distillate product is stored for further downstream uses or export.

3.2.2.8 Vanadium oxychloride removal

Vanadium oxychloride has similar thermal properties to titanium tetrachloride and is not separated upstream of distillation and, furthermore, would not be separated by conventional fractional distillation. Separation is achieved by the addition of an appropriate quantity of mineral or organic oil to the liquid being distilled. Vanadium oxychloride complexes with this oil and it is separated as a sludge, which is recycled back to solids separation, where it is removed from the process stream.

3.2.2.9 Oxidation

From storage, the liquid titanium tetrachloride and oxygen are preheated before mixing. Oxidation of the $TiCl_4$ to titanium dioxide and chlorine is carried out at between 900 – 1000 °C and 1500 – 2000 °C (overall range between 900 – 2000 °C), in either a plasma arc furnace or in a toluene-fired furnace, using oxygen injection [20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001]. The reaction involved is:

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

The oxidation phase is used to control the final quality of the TiO_2 crystal size to enable the product to be used as a pigment. Light metal chlorides (usually of aluminium and alkali metals) are used to aid this process. The reaction products are cooled and the titanium dioxide powder is collected in bag filters and the chlorine is recycled.

Oxygen supply and storage also need to be described. Of the five chloride plants covered in this document, four are supplied by pipeline with the production and storage of liquid oxygen on remote sites. One site has a local supplier with production and storage facilities on an adjacent site. The arrangement is supply on demand with only limited quantities of liquid storage to cover maintenance and unplanned downtime. The energy consumption and associated emissions are included in the LCA study – refer to Section 3.4.5.

3.2.2.10 Cooling and separation

The oxidation product stream is a mixture of chlorine, oxygen and titanium dioxide powder. After exiting the reactor, these are cooled by indirect water-cooling. The titanium dioxide is slurried with water and transferred to the finishing stage (see Section 3.3.2.9). Finishing treatment is similar to that of the sulphate process, including conditioning with additives.

Chlorine is separated in one of two ways. In the first (the older process), chlorine is absorbed/desorbed in liquid titanium tetrachloride before being returned to chlorination. In the second process, the chlorine from oxidation is directly recycled to chlorination [26, EIPPCB, 2003]. The basic processing stages are similar.

3.2.2.11 Absorption/desorption process

In the oxidation stage of the older process, the oxide is separated from the carrier gas, which is predominantly chlorine. The titanium dioxide is slurried in water and sent for finishing. The chlorine gas is drawn from the filters and then absorbed in liquid titanium tetrachloride in an absorption column. This liquid is stored, whilst the tail-gases pass to a scrubber train, to remove residual chlorine, with inerts passing to the main process stack.

Chlorine is recovered by desorption from the liquid titanium tetrachloride. The recycled chlorine is liquefied and stored or directly used in the chlorination section.

3.2.2.12 Direct chlorine recycling process

This process involves the direct recycling of chlorine from oxidation to chlorination, by operation of the oxidation reactors at a higher pressure than the chlorinators. It requires both the oxidation and chlorine process systems to be precisely synchronised. In both the new and old chlorine recovery processes, the gas solid separation systems are similar.

3.2.2.13 Finishing

This is common to both the chloride and sulphate process – refer to Section 3.3.2.9.

3.2.2.14 Abatement systems for gases

Off-gases from chlorination that include carbon monoxide (not present if a thermal oxidiser is in the process line – see below), carbon dioxide, with some hydrogen chloride and titanium tetrachloride, pass through the scrubbing train. Aqueous scrubbers absorb the HCl and then caustic scrubbing removes any chlorine that may 'slip' from the reaction stage.

This is achieved either by using a dedicated caustic scrubber with a backup caustic solution injection available or by direct injection of caustic into an aqueous scrubber in the event that chlorine is detected. When sodium hypochlorite is produced, it can either be sold or converted catalytically to salt water and oxygen before discharge.

It is practicable to produce sale grade hydrochloric acid in the first stage of scrubbing using demineralised water. This is done by a number of the European factories.

In the last few years, thermal converters have been installed to convert carbon monoxide and carbonyl sulphide (COS) in the tail-gas to carbon dioxide and sulphur dioxide, which reduces the toxicity of the discharge gases. There are specific variations at different sites:

- gases are scrubbed via 14 % and 28 % acid in scrubbers, then fed to a thermal converter, and then to a final scrubber or are directly sent to a final caustic scrubber. 28 % hydrochloric acid is sold as a co-product. No hypochlorite is sold. Waste caustic is neutralised with other effluents generated at the site
- the acid scrubber is followed by a thermal converter. No hydrochloric acid is sold. Hypochlorite is produced
- the acid scrubber is followed by a caustic scrubber or a thermal converter depending on the location. Hydrochloric acid is sold as a co-product. Sulphur is removed from the thermal converter stream for sale. No hypochlorite is produced.

Other venting and pressure reliefs from the process and storage areas (particularly chlorine) are usually scrubbed with caustic soda solution.

Refer also to the BREF on CWW, and to Section 8.2.4.1.

3.2.2.15 Abatement systems for solids

Waste solids from the chlorination stage, which consist of metal chlorides, coke and some ores, are neutralised in a chalk or lime slurry. The metals are precipitated and stabilised, and the filter cake is landfilled, while the aqueous filtrate is discharged to the appropriate aqueous environment.

Alternatively, the waste solids can also be treated by a special process to convert them into by-product hydrochloric acid and oxides. The conversion process involves roasting the chlorides in air to form HCl and leaving the oxides and unreacted coke as a solid residue. Steam may be raised with a waste heat boiler. The process has the potential for producing a relatively inert oxide and its possible use as an inert filler. It also allows for the chlorine content of the wastes to be utilised as hydrochloric acid. In the situation where the acid is sold, excess acid is usually neutralised.

Sand, salt (or granular TiO_2) may be used to scour titanium dioxide from the oxidation cooler. It is separated through lock hoppers or sand screens and sent to landfill, or re-used.

3.2.2.16 Abatement systems for liquids

Liquid emissions from the process are treated in a variety of ways. They can be an integral part of the gas and solids treatment systems, which normally has the effect of neutralising residual acidity and precipitating soluble metal chlorides. A significant proportion of the effluent can originate from the finishing section of the plant. This liquid consists of slightly alkaline solutions of alkali metal sulphates and chlorides together with suspended solids (TiO_2), which result from the coating process. These variations mean that the final effluent can be acidic or alkaline. In all cases, the consent limits of the effluent composition are influenced by the nature of the receiving media.

Refer also to the BREF on CWW, and to Section 8.3.4.

3.2.2.17 Co-products for sale or re-use

As described above, various emission treatment systems produce different co-products. They are sodium hypochlorite, hydrochloric acid, coke, iron chloride, metal oxide beads, $TiOCl_2$ solution, and sulphur cake (refer also to Section 7.4).

3.2.2.18 Purified titanium tetrachloride for sale

At least in one European TiO_2 plant based on the chloride process route, a minor part of the purified $TiCl_4$ is sold outside of the plant. To this end, a storage facility exists which is also subject to the provisions of the Seveso II Directive [23, The Council of the EU, 1996].

The co-production of the purified $TiCl_4$ is determined by several reasons, including market demand (also for the $TiCl_4$ used in the nucleation system in the titanium dioxide sulphate process), the possiblilty to lighten the process load in the back end of the plant (oxidation, cooling, separation), and to optimally adjust the energy balance in the plant.

3.2.3 Present consumption and emission levels – the chloride process

3.2.3.1 Current environmental performance

All data originate from the five European chloride sites and are for the year 1999 [20, CEFIC-TDMA, 2004]. Also, to bridge the gap between 1999 and the present time two case studies summaries of the environmental performance of two sites in 2002, one chloride and one sulphate, are given in Sections 3.2.3.7 and 3.3.3.6. Emissions to air and water, and waste to land, are given for the main stages of the process. Energy usage and water consumptions are given similarly but the process units are less detailed.

Unless stated otherwise, emissions and usages are given in kg per tonne of titanium dioxide pigment and, where appropriate, volume based emissions are included.

3.2.3.2 Raw materials consumption

3.2.3.2.1 Chlorination

Ore usage

The TiO_2 content of the main feedstocks range from 85 to 95 % and most sites use a selection of these materials in any one year. This makes direct comparison of the usages not very meaningful [20, CEFIC-TDMA, 2004]. A more useful comparison can be made by looking at the TiO_2 throughput. It is seen that the average consumption is 1075 kg TiO_2 (in feedstock) per tonne of TiO_2 pigment with a range of less than 5 %. Even here it is not valid to read too much into the maxima and minima data because they are made up of two or more different usages (including blends), which sometimes means that the usage is over or under estimated [20, CEFIC-TDMA, 2004].

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Feed	1075	1145	975

Table 3.8: The TiO_2 content of the main feedstocks
[20, CEFIC-TDMA, 2004]

The minimum figure in this box may cause some confusion, as it appears to indicate a reaction efficiency of over 100 %. However, as shown in Table 3.8, the results are reported as kg per tonne of TiO_2 pigment [20, CEFIC-TDMA, 2004]. For the record, the range of ore consumption is 1060 – 1189 kg/tonne pigment [20, CEFIC-TDMA, 2004]. The figures reflect a high physico-chemical efficiency of the chlorination process.

Chlorine usage

As illustrated in Table 3.9 below, chlorine gas is used as an intermediary in the process, the majority of which is recovered for re-use. However, some is used for chlorinating the impurities in the feedstock.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Chlorine	201	300	114

Table 3.9: **Chlorine usage**

The variation in usage is a direct function of the level of impurity in the feedstock that will undergo chlorination at the same time as the TiO_2.

Coke usage

The chlorination reaction requires carbon. It is supplied by high grade coke, which is continually added to the fluid bed.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Coke	366	429	285

Table 3.10: **Coke usage**

As illustrated in Table 3.10 above, coke usage can be a function of chlorinator design, in particular allowable fluidisation velocities. In recent years there has been a trend to run at higher velocities, which increases elutriation of unchlorinated particles (both ore and coke) and this reduces the need to shut down and purge these 'inerts'. The penalty for this is an increase in coke usage, which in turn offers the potential for recovery and re-use or sale of the recovered coke.

3.2.3.2.2 Solids separation and waste solid metal chlorides treatment

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Lime	137	220	91
Coal	90		

Table 3.11: **Lime and coal usage**

Various novel methods are used to reduce waste solids and convert them into useful co-products. One site uses coal in a fluid bed reactor to break down the metal chlorides into metal oxide beads and nominally 18 % hydrochloric acid.

This process is, however, technically very problematic and is currently under close examination as to whether, in its present form, it is both environmentally and economically effective [20, CEFIC-TDMA, 2004]. Iron chloride is extracted by another process (refer to Section 7.4). As given in Table 3.11 above, lime is used to neutralise the excess acid and to stabilise waste metal chlorides.

3.2.3.2.3 $TiCl_4$ purification

As given in Table 3.12 below, mineral or vegetable oil is used to complex the vanadium.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Oil	5	10	2

Table 3.12: Oil usage

3.2.3.2.4 Oxidation

As given in Table 3.13 below, pure oxygen is required to oxidise titanium tetrachloride. Some sites burn toluene [42, UBA-Germany, 2001] to achieve the heat input that others achieve by an electric arc (plasma) [20, CEFIC-TDMA, 2004]. In most cases, the oxygen supply gas is by pipeline with the liquefaction and storage plant sited remotely.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Oxygen	467	573*	395
Toluene	(Included in energy balance)		
* One site high figure for 1999 because of problems on chlorination that was solved by excess oxygen.			

Table 3.13: Pure oxygen used to oxidise titanium tetrachloride

3.2.3.2.5 Cooling and separation

Abrasive solids are used to scour the primary coolers, as shown in Table 3.14.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
Silica sand	49	73	26
Rock salt	16	29	7

Table 3.14: Abrasive solids usage

3.2.3.2.6 Finishing

Although finishing uses some raw materials, they are either not significant in this context or are covered in other sections (e.g. for caustic soda see box below).

3.2.3.2.7 Abatement systems for gases

Gases emitted from the above process are either scrubbed with HCl and the excess HCl is re-used or they are scrubbed with caustic soda solution and converted to sodium hypochlorite for resale or decomposition. The caustic soda solution usage is shown in Table 3.15. There are a number of different configurations of these systems.

Material	Mean kg/t TiO_2	Max kg/t TiO_2	Min kg/t TiO_2
NaOH	104	178	7

Table 3.15: Caustic soda solution usage

3.2.3.2.8 Abatement systems for liquids

No significant materials usage occurs here except the lime, which was included in Section 3.2.3.2.2 above.

3.2.3.3 Utilities consumption – energy and water

3.2.3.3.1 Energy

As given in Table 3.16 below, based on data compiled in 1999, the overall energy consumption for the production of a titanium dioxide pigment by the chloride process route was in the range of 17 to 29 GJ/t, with an average of approximately 25 GJ/t.

These data were also based on the application of a technique in which extra energy was used for chlorine absorption and desorption (at least 4 GJ/t pigment). This technique, however, is no longer in use in the EU titanium dioxide industry.

Even though a new set of data detailing energy usage in 2005 was not made available by the EU TiO_2 industry, given the progress made in energy efficiency, it has been reported that the upper level of overall energy usage for the chloride process is currently in the range of 21 to 23 GJ/t, and on average 17 to 22 GJ/t pigment [85, EIPPCB, 2004-2005] (refer to Table 3.29 below, which illustrates a clear downward trend of energy consumption between 1999 and 2002 in Greatham, UK).

Refer also to [42, UBA-Germany, 2001], where the energy demand in 2001 (average figures) for the chloride process route, illustrative for one plant in Leverkusen, Germany, was estimated at the level of 18.8 GJ/t and from this for TiO_2 manufacture 6.1 GJ/t and for follow-up treatment 12.7 GJ/t pigment.

Table 3.16 illustrates energy consumption in 1999 of the main production areas [20, CEFIC-TDMA, 2004]. These were site usages of energy, which did not include the energy used in the production of raw materials (ore, oxygen, etc.). These had been taken into account in the LCA study – see Section 3.4.5 [20, CEFIC-TDMA, 2004].

Site/process	Chloride (averages)	Chloride (maximum)	Chloride (minimum)
Date/year	1999	1999	1999
Energy TiO_2 usage ore preparation to oxidation (*)			
Electricity GJ/t	2.3	3.3	1.5
Steam GJ/t	2.4	7.6	1.3
Gas GJ/t	3.2	6.6	1.3
Energy: TiO_2 usage finishing			
Electricity GJ/t	2.6	5.7	0.8
Steam GJ/t	6.9	10.4	7.1
Gas GJ/t	5.7	13.2	2.8
Energy: effluent treatment			
Electricity GJ/t	1.7	2.9	0.5
Steam GJ/t	0.0	0.0	0.0
Gas GJ/t	0.0	0.0	0.0
Heavy fuel oil GJ/t	0.0	0.0	0.0
Overall total energy per site	**24.8**	**28.7**	**17.4**
(*) Average and maximum energy consumption figures 1999 up to oxidation include the operation of indirect, more energy intensive chlorine recycling at some of the sites. This technique is no longer in use in the EU TiO_2 industry.			

Table 3.16: Energy consumption in TiO_2 production based on the chloride process in 1999 [20, CEFIC-TDMA, 2004]

It should also be noted [20, CEFIC-TDMA, 2004] that different sites use different sources of energy to perform the same function, hence the above 1999 data rows are the average, maxima and minima for all the sites which helps to explain the variations [20, CEFIC-TDMA, 2004].

As with the sulphate process the energy usage analysis has been simplified [20, CEFIC-TDMA, 2004]. As explained earlier, there is relatively little energy required for effluent treatment since this is effectively carried out at the feedstock production site during the increase in TiO_2 content of the feedstock [20, CEFIC-TDMA, 2004].

3.2.3.3.2 Water

As seen in Table 3.17, there is a wide disparity in water usage that is not easily explained. It is probable that local availability of water has some influence [20, CEFIC-TDMA, 2004]. Water usage is quite a complex issue and direct intersite comparison is difficult, however, it may help to set the targets for the reduction of annual water usage, including water re-use.

Site/process	**Chloride averages (m^3/tonne)**	**Max. chloride (m^3/tonne)**	**Min. chloride (m^3/tonne)**
Date/year	1999	1999	1999
Treated	21.49	43.14	10.95
Non treated	11.0	17.0	0.0
Treated water for steam generation	1.82	3.65	0.76
Total water per site	**34.5**	**48.0**	**22.6**

Table 3.17: Water consumption for the chloride process

The above data are the average, maxima and minima for all the sites, which helps to explain the variations, and means that the totals quoted are not necessarily the sums of the columns [20, CEFIC-TDMA, 2004].

3.2.3.4 Emissions to air

Because of the nature of the main process, most of the gaseous effluents pass through a common scrubbing system and exit into the atmosphere via a single stack. For the purposes of assessing the effectiveness and efficiency of the primary processing units, the main gaseous emissions have been allocated to their most probable source.

3.2.3.4.1 Raw material import and preparation

Dust is the major issue here and the preparation stage is an intermittent source of dust emissions. There is a wide disparity in the frequency of measurements on different sites due to their particular regimes. For example, one site does not do routine measurements but personnel monitors are used. This makes the combination of the data difficult. Dust and NO_X emissions are given in Table 3.18.

Emissions to air		
Emitted substance	**Dust**	**NO_X**
Treatment method	Bag filters	
kg/t TiO_2 (average)	**0.002**	**0.008**
kg/t TiO_2 (max)	0.005	0.016
kg/t TiO_2 (min)	0.000	0.000
Collection period	1999	1999
Number of data (average)	91750	4000
Typical volume based value	**Dust**	**NO_X**
mg/Nm^3 (average)	**18**	**54**

Table 3.18: Dust and NO_X emissions – TiO_2 production, the chloride process [20, CEFIC-TDMA, 2004]

NO_X is emitted in the exhaust gas of the heater when there is a need to dry the feedstock. One site dries the recovered ore and coke.

3.2.3.4.2 Chlorination

Emissions to air from the chlorination stage are given in Table 3.19 below.

Emissions to air							
Emitted substance	**Cl_2**	**CO**	**COS**	**CO_2**	**SO_2**	**NO_X**	**HCl**
Treatment method	Oxidiser followed by water, acid or lime scrubbing						
kg/t TiO_2 (average)	**0.003**	**159**	**2.39**	**923**	**1.14**	**0.10**	**0.10**
kg/t TiO_2 (max)	0.008	297	3.99	1790	4.00	0.12	0.16
kg/t TiO_2 (min)	0.000	0	0.00	56	0.01	0.07	0.05
Collection period	1999	1999	1999	1999	1999	1999	1999
No of data (average)	18	15	8	11	11	11	192
Typical volume based value	**Cl_2**	**CO**	**COS**	**CO_2**	**SO_2**	**NO_X**	**HCl**
mg/Nm^3 (average)	**1**	**1570**	**21**	**49344**	**286**	**51**	**35**

Table 3.19: Emissions to air from chlorination – TiO_2 production, the chloride process [20, CEFIC-TDMA, 2004]

Chlorine emissions are rare and are controlled by water or caustic scrubbing, usually in packed spray towers, for maximum efficiency. Small quantities of HCl remain in the off-gas. All sites now have thermal oxidisers for burning CO and COS.

Heat generated at the oxidiser stage is recovered to raise steam. The data also reflect the commissioning and start up of some units in the year of measurement (1999). Natural gas is used for burning COS and CO, which results in emissions of NO_X, CO_2 and SO_2 [20, CEFIC-TDMA, 2004].

It should also be noted, in particular as far as SO_2 emissions are concerned, that the 1999 data given above in Table 3.19 were representative for a sulphur content of 0.8 – 1.0 % in the input pet coke used in the process [20, CEFIC-TDMA, 2004]. In turn, it is reported that in 2005 it is possible only to buy coke with a sulphur content of 1.0 to 1.8 %, which results in higher SO_2 emissions from the process [85, EIPPCB, 2004-2005].

3.2.3.4.3 Solids separation

Emitted substance	**HCl**
Treatment method	Acid scrubbing
kg/t TiO_2 (average)	**0.0037**
kg/t TiO_2 (max.)	0.0070
kg/t TiO_2 (min.)	0.0003
Collection period	1999
No of data (average)	2

Table 3.20: Data on hydrogen chloride emissions

Data on hydrogen chloride emissions given in Table 3.20 are from one site – no volume based data available.

3.2.3.4.4 Waste solid metal chlorides treatment

Emissions to air			
Emitted substance	**NO_X**	**HCl**	**Dust**
Treated method	Combustion	scrubber	None
kg/t TiO_2 (average)	**1.40**	**0.6**	**0.5**
Collection period	1999	1999	1999
No of data (average)	4	Continuous	4

Table 3.21: Emissions to air from waste solid metal chlorides treatment

As seen in Table 3.21, the emissions are all from the site that treats its metal chlorides in a coal fired fluid bed, where the exit gases are quenched and scrubbed. No volume based values are available.

3.2.3.4.5 Condensation

No gaseous emissions are allocated to condensation but it is likely that some residual HCl originates from here.

3.2.3.4.6 Waste gas treatment

See Section 3.2.3.4.9 below – Abatement systems for gases.

3.2.3.4.7 Oxidation

All sites use either gas or steam to preheat the tetrachloride feed to oxidation. The emission data from one site are given in Table 3.22.

Emissions to air	
Emitted substance	**SO_2**
Treatment method	None
kg/t TiO_2 (average)	**0.14**
Collection period	1999
No of data (average)	6
Typical volume based value	SO_2
mg/Nm^3 (average)	2

Table 3.22: Emissions to air from oxidation

3.2.3.4.8 Finishing

Dust is the main emission of concern and invariably strict control measures are in place to keep them to a minimum. This is as much an occupational hygiene issue as an environmental one. Dust and NO_X emissions from the finishing section are given in Table 3.23.

Emissions to air		
Emitted substance	**Dust**	**NO_X**
Treatment method	Bag filters	
kg/t TiO_2 (average)	**0.158**	**0.020**
kg/t TiO_2 (max.)	0.400	0.020
kg/t TiO_2 (min.)	0.002	0.020
Collection period	1999	1999
No of data (average)	7	4
No of data (max.)	18	4
No of data (min.)	1	4
Typical volume based value	Dust	NO_X
mg/Nm³ (average)	**21**	

Table 3.23: Dust and NO_X emissions, finishing section – TiO_2 production, the chloride process [20, CEFIC-TDMA, 2004]

3.2.3.4.9 Abatement systems for gases

In principle, there are two abatement systems used. Both use scrubbing trains, the difference is the liquid medium one uses caustic soda and produces hypochlorite as a co-product. The other uses water and produces hydrochloric acid for sale or re-use. The choice of which system is preferred, depends on the local market for co-products.

3.2.3.5 Emissions to water

3.2.3.5.1 Waste solid metal chlorides treatment

Emissions of metals to water are presented in Table 3.24.

Emissions to water				
Treatment method	**Neutralisation as required**			
Emitted substance	**Fe**	**Hg**	**Cd**	**Other metals***
Collection period	1999	1999	1999	1999
No. of data (average)	75	130	156	209
No. of data (max)	183	365	365	365
No. of data (min)	12	52	52	52
kg/t TiO_2 (average)	**2.3**	**8.56 E $^{-06}$**	**5.76 E $^{-05}$**	**1.334**
kg/t TiO_2 max	8.8	2.00 E $^{-05}$	1.80 E $^{-04}$	2.000
kg/t TiO_2 min	0.0001	1.60 E $^{-08}$	8.00 E $^{-08}$	0.003
Typical volume based concentrations	**Fe**	**Hg**	**Cd**	**Other metals***
mg/litre	**0.56**	**0.0002**	**0.0012**	**32.6**

Note: Data from the German TiO_2 plant, based on the chloride process, are broadly consistent with the above-mentioned data, as the emission of waste solid metal chlorides after neutralisation are reported to be as follows: Fe – 0.011 kg/t TiO_2; Hg – 2.2 E $^{-07}$ kg/t TiO_2; Cd – 2.2 E $^{-07}$ kg/t TiO_2; Other metals – 0.0025 kg/t TiO_2.

* Other metals: Manganese (Mn), Vanadium (V), Titanium (Ti), Zinc (Zn), Chromium (Cr), Lead (Pb), Nickel (Ni), Copper (Cu), Arsenic (As). It should be noted that in the group of other metals, Ti and Mn are much less harmful for the environment than the remaining metals listed above. The emission level of the remaining metals (V, Zn, Cr, Pb, Ni, Cu, As) is estimated at <0.1 kg/t TiO_2 pigment [85, EIPPCB, 2004-2005].

Table 3.24: Emissions of metals to water – TiO_2 production by the chloride route [20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001]

3.2.3.5.2 Condensation and gas scrubbing

Emissions of hydrochloric acid and suspended solids to water is given in Table 3.25.

Emissions to water		
Treatment method	**Lagoon**	
Emitted substance	**HCl**	**Suspended solids**
Collection period	1999	1999
No of data (average)	365	365
kg/t TiO_2 (average)	**16**	**0.36**

Table 3.25: Emissions of hydrochloric acid and suspended solids to water

This is information from one site only and it should be noted that the HCl figure is relatively high and modifications are already in hand to reduce it. No volume-based concentrations are available.

3.2.3.5.3 Finishing

Emissions of suspended solids and chlorides to water are given in Table 3.26.

Suspended solids (which basically are inert titanium dioxide particles and, on some sites, solids from imported river or seawater) are the only significant aqueous emission attributed to this section, however for editing convenience, chloride ion values for the liquid effluent are also included here. It can be noted that a certain quantity of soluble sulphate ions are released from the finishing section which come from the coating process in the form of sodium sulphate.

Emissions to water		
Treatment method	**Filtration, settling**	
Emitted substance	**Suspended solids**	**Chlorides**
Collection period	1999	
No. of data (average)	98	
No. of data (max)	183	
No. of data (min)	12	
kg/t TiO_2 (average)	**4.64**	**164**
kg/t TiO_2 max	11.10	330
kg/t TiO_2 min	0.57	38
Typical volume based concentration	**Suspended solids**	**Chlorides**
mg/litre	5.23	185

Table 3.26: Emissions of suspended solids and chlorides to water – TiO_2 chloride process [20, CEFIC-TDMA, 2004]

It should be also noted that, as compared to the range of emissions of chlorides to water, i.e. 38 to 330 kg/t TiO_2 pigment characteristic for the chloride process route as given in Table 3.13 above, the TiO_2 Harmonisation Directive 92/112/EEC limits emissions of chlorides to water depending on the titanium feedstock used, namely:

- 130 kg chlorides/t TiO_2 pigment for natural rutile as raw material
- 228 kg chlorides/t TiO_2 pigment for synthetic rutile
- 450 kg chlorides/t TiO_2 pigment for slag used as raw material in the production process.

3.2.3.5.4 Abatement systems for gases

There are no direct emissions from this section, however, it should be noted that aqueous emissions from gas scrubbers at the sites form part of liquid effluent stream.

3.2.3.5.5 Abatement systems for liquids

The liquids concerned are hydrochloric acid or caustic soda solution. It can be seen from the above that most processes are designed so that the emission of these substances to the aqueous environment is minimised.

3.2.3.6 Solid wastes

3.2.3.6.1 Chlorination

Waste to land	
Emitted substance	Inerts (solids)
kg/t TiO_2 (average)	224

Table 3.27: Waste sent to landfill from the chlorination unit

Table 3.27 reflects one site where the blow-over from the chlorination section is sent to landfill. Some recovery of waste is expected for 2000.

3.2.3.6.2 Waste solid metal chlorides treatment

Waste to land	
Treatment method	Neutralisation or roasting
Emitted substance	Solids
kg/t TiO_2 (average)	397
kg/t TiO_2 max	660
kg/t TiO_2 min	99

Table 3.28: Emission levels of solids from metal chlorides treatment by neutralisation or roasting

Table 3.28 gives the emission levels of solids from metal chlorides treatment by neutralisation or roasting. Lime is usually used to render the heavy metals insoluble so the material is suitable for disposal to land. Some sites separate unreacted coke for sale or re-use, others extract the iron component as ferrous chloride for sale.

3.2.3.6.3 Distillation and vanadium oxychloride removal

Although this section technically produces solids for disposal, the material is internally transferred and it is combined with waste from solid metal chloride treatment – see Section 3.2.3.6.2.

3.2.3.7 Environmental performance – Greatham Works 2002

The purpose of this case study is to help bridge the gap after 1999 when the original performance data was collected. Year 2002 saw the closure of the older Black End plant in August and the start-up of the new ICON 2 (ICON = Integrated Chlorination and Oxidation) titanium dioxide plant in October. Since the closure of the Black End plant, considerable progress has been made on the inventory of hazardous chemicals and work has commenced on demolition.

Figure 3.3 gives the overall production balance for 2002 in Greatham, illustrating major inputs and outputs from the titanium dioxide production process based on the chloride process route.

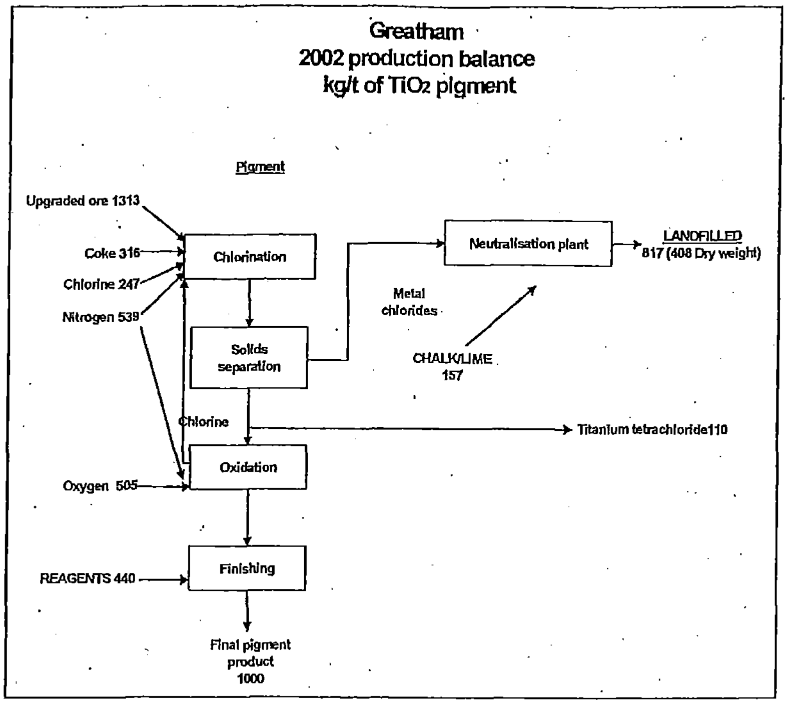


Figure 3.3: Main raw materials inputs and production outputs for the Greatham site for 2002 [20, CEFIC-TDMA, 2004]

Most emissions to air and water showed a reduction compared to 2001. This is partially explained by a small reduction in production from the site due to the change-over from the Black End to ICON 2.

Hazardous waste disposal shows a significant increase, however, most of this is material removed from the (shut-down) Greatham Black End as part of the decontamination/demolition programme.

Improvements achieved in 2002:

- total neutralisation plant – all acidic liquid effluent from the site is now treated before discharge, to neutralise residual acid
- ozone depleting substances – the black End refrigeration plant was decommissioned and the refrigerant was removed.

Detailed annual emissions 1999 – 2002 in kg per tonne of TiO_2, recorded in the Greatham Works titanium dioxide plant based on the chloride process are given in Table 3.29.

	kg/tonne 1999	kg/tonne 2000	kg/tonne 2001	kg/tonne 2002
Discharges to water				
Hydrochloric acid	16	13	13	12
Titanium (Ti)	0.8	0.6	0.5	0.6
Suspended solids	0.6	0.5	0.4	0.5
Manganese (Mn)	0.6	0.6	0.4	0.5
Iron (Fe)	0.28	0.55	0.67	0.61
Vanadium (V)	0.03	0.03	0.03	0.02
Chromium (Cr)	0.003	0.004	0.004	0.002
Zinc (Zn)	0.006	0.007	0.009	0.005
Nickel (Ni)	0.019	0.015	0.004	0.001
Lead (Pb)	0.011	0.009	0.002	0.000
Copper (Cu)	0.003	0.003	0.006	0.001
Arsenic (As)	0.0001	0.0001	0.0001	0.0000
Cadmium (Cd)	0.00018	0.00013	0.00012	0.00001
Mercury (Hg)	0.00007	0.00001	0.00000	0.00000
Chlorinated organic compounds	0.00041	0.00027	0.00025	0.00025
Emissions to air				
Carbon monoxide	181	116	65	83
Carbonyl sulphide	3.2	1.9	1.3	0.4
Nitrogen oxides (as NO_2)	1.2	1.3	1.2	1.2
Particulates	0.4	0.1	0.1	0.1
Sulphur dioxide	0.3	0.2	0.1	0.1
Hydrogen chloride	0.2	0.0	0.0	0.0
Chlorine	0.00041	0.00054	0.00050	0.00012
Hydrogen sulphide	0.1	0.1	0.0	0.0
Carbon dioxide (ex process)	437	487	729	576
Carbon dioxide (ex combustion)	1304	1090	1110	989
Carbon dioxide (from bought in energy)	609	588	561	540
Wastes to land				
Non-hazardous waste	729	785	881	962
Hazardous waste to land/incineration	0.5	1.8	0.9	1.8
Resource consumption				
Water usage m^3	38	32	31	32
Energy usage GJ	29	26	26	23

Table 3.29: Emissions 1999 – 2002 in the Greatham Works TiO_2 plant, the chloride process [20, CEFIC-TDMA, 2004]

3.2.4 Techniques to consider in the determination of BAT – the chloride process

This section sets out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of this document. Management systems, process-integrated techniques and end-of-pipe measures are included, but a certain amount of overlap exists between these three when seeking the optimum results.

Prevention, control, minimisation and recycling procedures are considered as well as the re-use of materials and energy.

Techniques may be presented singly or as combinations to achieve the objectives of IPPC. Annex IV to the Directive lists a number of general considerations to be taken into account when determining BAT and techniques within this section will address one or more of these considerations. As far as possible a standard structure is used to outline each technique, to enable comparison of techniques and an objective assessment against the definition of BAT given in the Directive.

The content of this section is not an exhaustive list of techniques and others may exist or be developed which may be equally valid within the framework of BAT. Generally a standard structure is used to outline each technique, as shown in Table 3.30:

Type of information considered	Type of information included
Description	Technical description of the technique
Achieved environmental benefits	Main environmental impact(s) to be addressed by the technique (process or abatement), including emission values achieved and efficiency performance. Environmental benefits of the technique in comparison with others
Cross-media effects	Any side-effects and disadvantages caused by implementation of the technique. Details on the environmental problems of the technique in comparison with others
Operational data	Performance data on emissions/wastes and consumption (raw materials, water and energy). Any other useful information on how to operate, maintain and control the technique, including safety aspects, operability constraints of the technique, output quality, etc.
Applicability	Consideration of the factors involved in applying and retrofitting the technique (e.g. space availability, process specific)
Economics	Information on costs (investment and operation) and any possible savings (e.g. reduced raw material consumption, waste charges) also as related to the capacity of the technique
Driving force for implementation	Reasons for implementation of the technique (e.g. other legislation, improvement in production quality)
Example plants	Reference to a plant where the technique is reported to be used
Reference literature	Literature for more detailed information on the technique

Table 3.30: Information breakdown for each technique described in this section

Reference is also made here to Section 8.9, providing key information on the Environmental Management System (EMS) which is a tool for IPPC installations that operators can use to address the design, construction, maintenance, operation and decommissioning issues in a systematic demonstrable way.

Techniques broadly applicable in the chemical industry, described in the BREF on Common Waste Water and Waste gas Treatment/Management Systems in the Chemical Sector, are not included in this section (refer to the BREF on CWW).

3.2.4.1 Raw material import and preparation

3.2.4.1.1 Dry titanium dioxide ore

Description
The ore needs to be in a dry state and with a low moisture content prior to processing. Ensuring that the ore is delivered to the site in a dry state may require collaboration with upstream suppliers and those who transport and handle the ore. Covered storage prevents wetting of the ore by rain. Drying of the ore (typically synthetic rutile) is not normally required in the European titanium dioxide plants based on the chloride process route, but, if required, would entail the use of energy with associated emissions of combustion products. Low moisture content in the ore reduces chlorine losses in the downstream chlorination section due to the undesirable formation of the HCl and results in a higher yield of titanium ore to titanium tetrachloride.

Achieved environmental benefits
The higher the yield of the TiO_2 ore to $TiCl_4$, the lower the overall impact of titanium dioxide production on the environment.

Cross-media effects
Increased amounts of dust may be expected when the titaniferous ore is handled in a dry state, however, this is restricted by enclosed handling and storage – refer also to Section 3.2.4.1.2.

Operational data
No information submitted on the acceptable levels of moisture content in the titaniferous ores used for the production of TiO_2 based on the chloride process. Although there is no clear equivalence between the chloride and sulphate processes, and there are quite different reasons for keeping the titanium ore dry prior to its further processing, reference is made here to the information source on the sulphate process [42, UBA-Germany, 2001], quoting that the required moisture content in the ore prior to processing is below 0.1 %.

Applicability
Applicable to all plants using the chloride process route.

Economics
No data submitted.

Driving force for implementation
Higher performance of the whole process due to the avoided chlorine losses in the chlorination section and, hence, the higher yield of titanium ore in the process. Additionally, reduced or eliminated emissions from drying the ore.

Example plants
Titanium dioxide plant in Greatham, UK.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.1.2 TiO_2 ore dedusting systems

Description
The main issue in feedstock preparation on the site of a titanium dioxide plant is dust emission during the movement of dry bulky materials. Normally this is controlled by handling the ore in closed systems kept under reduced pressure with the dust being collected in cyclones for re-use. Cyclones are more robust depending on their proper design. The cyclones may be followed by reverse pulse bag micro-filters, which are likely to minimise dust emissions, provided they are supported by an efficient monitoring and maintenance regime. High quality maintenance routines are necessary to minimise dust emissions from worn or badly fitted filter socks. Continuous dust measurement systems are an obvious aid to minimising feedstock losses.

Achieved environmental benefits
Minimisation of TiO_2 ore dust emissions in the raw materials preparation section.

Cross-media effects
No side effects or disadvantages caused by implementation of this technique are reported.

Operational data
As presented in Section 3.2.3.4.1 and, in particular, in Table 3.18. Average specific emissions of dust to air are at the level of 0.002 kg/t TiO_2, the maximum emission of dust to air being reported at the level of 0.005 kg/t TiO_2 produced.

Applicability
Applicable to all plants using the chloride process route.

Economics
No data submitted.

Driving force for implementation
Standard requirements of dust emissions to air.

Example plants
Titanium dioxide plant in Greatham, UK.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.1.3 Low sulphur content in feedstock granular coke

Description
Low sulphur coke is required in a granular form suitable for fluidisation in the chlorination process. The sulphur content of the coke influences the COS concentration and subsequently the SO_2 concentration in the off-gas from the thermal oxidisers. However, the availability of low sulphur coke is limited, as the average sulphur content in the coke was reported to have increased from 0.8 – 1.2 % in 1999 to 1.0 – 1.8 % in 2005.

Achieved environmental benefits
Reduced emissions of SO_2 from the TiO_2 plant.

Cross-media effects
No side effects or disadvantages caused by implementation of this technique are expected to be encountered in the titanium dioxide industry.

Operational data
Refer to data included in Sections 3.2.2.14 and 3.2.3.4.2. Specific emissions of SO_2 to air are in the range of 0.01 to 4.00 kg/t TiO_2.

Applicability
Technique applicable to all plants using the chloride process route.

Economics
No information submitted.

Driving force for implementation
Standard requirements of COS and SO_2 emissions to air.

Example plants
Titanium dioxide plant in Greatham, UK.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [85, EIPPCB, 2004-2005].

3.2.4.1.4 Low chlorine inventory

Description
Chlorine is recycled within the process, with any 'make up' chlorine usually being imported by tanker as a liquid. Afterwards, chlorine is delivered to the chlorine storage in the TiO_2 plant either by a rail pipeline or by road, depending on the site location. For the storage and the handling of chlorine, refer to the BREF on the Chlor-Alkali Manufacturing Industry.

The hazardous nature of chlorine is the main property, which influences the basic design of the titanium dioxide chloride process. This means that the initial primary stages of the process (the 'black end') are totally enclosed and of high integrity. In Europe, all TiO_2 plants based on the chloride process route are controlled by both the Seveso II Directive [23, The Council of the EU, 1996] and by the Titanium Dioxide Harmonisation Directive [21, The Council of the EU, 1992], which require detailed hazard assessments to be carried out and minimal emissions of chlorine into the environment.

Good production and maintenance planning, together with a proper relationship with the chlorine suppliers, is required to maintain a low chlorine inventory. A minimum chlorine inventory is an obvious goal in order to minimise potential harm in the event of a major chlorine release.

Achieved environmental benefits
In the case of any accidental release of chlorine from storage, a lower inventory will result in a lower impact on the environment as a result of the release.

Cross-media effects
A minimum chlorine inventory involves more frequent handling operations of liquid chlorine transport from the chlorine supplier and liquid chlorine loading into chlorine storage in the TiO_2 plant, which may potentially result in uncontrolled local emissions of chlorine gas (leaking valves, flanges, gaskets, etc.).

Excellent co-operation between the liquid chlorine supplier and the TiO_2 producer is required to maintain a minimum stock on site.

Operational data
No information submitted.

Applicability
Applicable to all plants using the chloride process route.

Economics
No data provided.

Driving force for implementation
The maximum degree of safety both of the operator's staff and of the human beings living in the proximity of the TiO_2 plant based on the chloride process route.

Example plants
Titanium dioxide plant in Greatham, UK.
Titanium dioxide plant in Stallingborough, UK.
Titanium dioxide plant in Langebrugge, Belgium.
Titanium dioxide plant in Leverkusen, Germany (the chloride process route).
Titanium dioxide plant in Rotterdam, the Netherlands.

Reference literature
[20, CEFIC-TDMA, 2004], [6, CEFIC, 2002], [26, EIPPCB, 2003], [70, Environment Agency, 1999], [12, European Environment Agency, 2004], [75, J. A. Lee, 1985], [21, The Council of the EU, 1992], [23, The Council of the EU, 1996], [11, The Council of the EU, 1996], [42, UBA-Germany, 2001], [78, World Bank, 1991].

Refer also to the BREFs on:

- CAK (Chlor-Alkali Manufacturing Industry)
- MON (General Principles of Monitoring)
- ESB (Emissions from Storage)
- CV (Industrial Cooling Systems)
- CWW (Common Waste Water and Waste gas Treatment/Management Systems in the Chemical Sector).

3.2.4.2 Chlorination

Description
Steady state operation of a fluidised-bed reactor to sustain a good temperature and composition control to avoid chlorine slip and downtime from sintered beds is the best measure to minimise environmental impacts from chlorination. In modern titanium dioxide plants based on the chloride process, this section uses a pressurised chlorinator fed directly with recycled chlorine at an optimum fluidisation velocity. Modern plants have been redesigned with rapid maintenance in mind to minimise unplanned downtime. This, combined with modern low volume systems, helps to minimise losses. Chlorinators should be designed for ease of maintenance to maximise overall process efficiency.

Achieved environmental benefits
Steady state operation of the chlorination section allows for:

- maximising chlorine utilisation in the chlorine recovery loop and a higher chlorine yield to titanium tetrachloride in one reaction pass, thus increasing overall plant efficiency and reducing the impact on the environment
- keeping a fluidised-bed reactor in operation for an extended time, thus minimising the number of stoppages required to replace the reactor bed, and reducing the impact on the environment.

Cross-media effects
Intermittent purge of solids from the reactor (mainly unchlorinated particles of the ore and coke). Normally, the re-use of unchlorinated particles is problematic because of the fine particle size and impurity contamination.

Operational data
All raw materials, including coke, should be dry and free from volatile substances, in order to avoid chlorine losses by the formation of HCl. The chlorine conversion rate is approx. 98 - 100 %, while the TiO_2 content in the raw material is converted to a rate of approx. 90 - 100 %. The chlorination temperature is approximately 1000 °C, in which most of the generated metal chlorides are gaseous, with the exception of Mg and Ca chlorides. Therefore, the raw materials should not exceed certain limit values of Mg and Ca, in order to avoid their sticking in the fluidised bed. The chlorination reactors may require total bed replacement about once a year. The gases leaving the chlorinator contain Cl_2, CO, COS, and HCl. The train for waste gas treatment contains multistage washing, combustion and, sometimes, desulphurisation [42, UBA-Germany, 2001], refer to Section 3.2.4.5.

All sites have thermal oxidisers for burning CO and COS, sometimes with the heat recovered to raise steam. Heat recovery as steam has an obvious environmental advantage but periodic descaling of the boiler tubes causes the abatement unit to be out of action for 10 – 15 % of the plant operational time.

Natural gas is used for burning COS and CO, which results in the emissions of CO_2, SO_2, and NO_X. For more detailed information on the chlorination process, as well as on emissions to air and wastes to land from the chlorination stage, refer to Sections 3.2.2.2, 3.2.3.2.1, 3.2.3.4.2, and 3.2.3.6.1.

Applicability
Steady state operation of the chlorination section, equipped with modern fluidised-bed reactors, are applicable to all plants using the chloride process route.

Economics
No information submitted.

Driving force for implementation
The overall process efficiency increases, leading to the reduction of TiO_2 manufacturing costs, and lessening the impact of TiO_2 production on the environment.

Example plants
Titanium dioxide plant in Greatham, UK.
Titanium dioxide plant in Stallingborough, UK.
Titanium dioxide plant in Langebrugge, Belgium.
Titanium dioxide plant in Leverkusen, Germany (the chloride process route).
Titanium dioxide plant in Rotterdam, the Netherlands.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [48, W. Buchner et al, 1989]:

3.2.4.3 Solids separation – coke and ferrous chloride recovery

Description
Fine solids of residual TiO_2, SiO_2, and coke as well as gaseous metal chlorides are discharged from the reactor together with the $TiCl_4$ and the residual reaction gases. These are cooled by the addition of cold $TiCl_4$, upon which the main part of other metal chlorides condenses and can be separated together with the solids present in the main gas stream of the reactor. Recovery of unreacted ore and coke may be a potential option for systems with a high carryover of these materials in the gas stream.

Deeper analysis of the environmental impact and a cost-benefit assessment would be necessary to ensure, on balance, that the recovery of unreacted ore and coke is justified. Typically, at this stage of the process, coke and ferrous chloride solution are separated, which can then be sold as a by-product, provided a local market can be developed (refer also to Section 7.4).

Achieved environmental benefits
Separation of residual coke and ferrous chloride that would otherwise be the waste solid materials directed to a landfill and for waste water treatment.

Cross-media effects
Additional energy requirements and the consumption of hydrochloric acid (refer to Section 7.4).

Operational data
As described in Section 7.4, the recovery of 942 kg of 20 % $FeCl_2$ solution per tonne of TiO_2 produced has been reported. No data on the degree of coke recovery was submitted.

Applicability
In principle, this technique is applicable to all plants using the chloride process route.

Economics
No information submitted.

Driving force for implementation
Reduction of waste materials directed to a landfill and for the waste water treatment.

Example plants
Titanium dioxide plant in Leverkusen, Germany.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [90, CEFIC-INCOPA, 2004].

3.2.4.4 Waste solid metal chlorides neutralisation with chalk or lime

Description
After the optional treatment of solids and metal chlorides to recover both coke and $FeCl_2$ from the waste stream, solid metal chlorides are usually neutralised in a chalk or lime slurry which renders the residual metals insoluble. The metals are precipitated and stabilised, and the filter cake is landfilled, while the filtrate is discharged to the appropriate aqueous environment.

Where the neutralised metal chlorides are disposed of to landfill, tight pH control of neutralisation and leachate checks from the landfill site are necessary to guarantee the waste metal ions are stabilised and do not contaminate the water table.

The off-gas from the treatment of solid metal chlorides is cleaned in a scrubber before being discharged to the atmosphere (refer to Section 3.2.3.4.3). The acid wash-water from the scrubber is recycled to the main section for the treatment of solid metal chlorides.

Achieved environmental benefits
The neutralisation of solid metal chlorides with chalk or lime renders the residual metals insoluble, before their disposal as a solid waste to landfill. It should be noted, that it is necessary to use high purity chalk or lime.

Cross-media effects
Additional lime usage in the range of 91 to 220 kg/t TiO_2.

Operational data
In Sections 3.2.3.5.1 and 3.2.3.6.2, as well as in Table 3.29, specific emission figures from one site in Germany (Leverkusen) are reported.

It should be noted, that solid emissions also depend on the abatement system for liquids used in the titanium dioxide plants based on the chloride process route. Relevant data on waste to land are also included in Section 3.2.4.10.3.

Applicability
Applicable to all plants using the chloride process route.

Economics
No data submitted.

Driving force for implementation
The metal ions are stabilised and when landfilled they do not contaminate the water table.

Example plants
Titanium dioxide plant in Greatham, UK.
Titanium dioxide plant in Leverkusen, Germany.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.5 $TiCl_4$ condensation and waste gas treatment

Description
In this step the majority of the titanium tetrachloride is separated from the gas stream by multistage cooling/condensation to temperatures below 0 °C. Carefully designed high efficiency condensers are used at this stage. Depending on the process conditions, the CFC-free cooling system usually uses ammonia or brine.

The gas stream – containing traces of $TiCl_4$, CO, CO_2, COS, HCl, and Cl_2 – is then passed to the multistage waste gas treatment unit, in which several consecutive operations are performed to remove (Cl_2) and utilise chlorine compounds (HCl, NaClO), to desulphurise off-gas (COS) to possibly extract sulphur, and finally, to thermally convert CO (and COS) contained in the off-gas to CO_2, before the off-gas is released to the atmosphere.

In principle, there are two abatement systems used. Both use scrubbing trains, the difference is the liquid medium one uses caustic soda and produces sodium hypochlorite as a co-product. The other uses water and produces hydrochloric acid for sale or re-use.

Specific configurations of the multistage waste gas treatment unit used in the titanium dioxide industry based on the chloride process route are:

- absorption of chlorine compounds, yielding 28 % HCl, which is sold, followed by a thermal combustion of CO and COS in the off-gas, and then a final scrubbing of the off-gas with the solution of caustic soda
- the acid scrubber is followed by a thermal converter. No hydrochloric acid is sold. Sodium hypochlorite is produced at the site
- the acid scrubber is followed by a caustic scrubber or thermal converter depending on the location. Hydrochloric acid is sold as a co-product. Sulphur is removed from the thermal converter stream for sale. No sodium hypochlorite is produced.

Thermal converters or oxidisers are used to render the carbon monoxide and carbonyl sulphide (COS) in the tail-gas harmless. There are two similar systems. In one, the gases are converted to carbon dioxide and sulphur dioxide (the latter is scrubbed with an alkali). In the other, the end-products are carbon dioxide and sulphur. Thermal oxidisers need careful design and operation because it is critical to avoid acid corrosion (particularly triggered by the over-cooling of the off-gas, and therefore, its condensation and subsequent hydrochloric acid formation).

There are a number of different scrubbing systems, which can be taken into consideration. Their efficacy is dependent on local circumstances, the availability of markets and the internal usage of co-products.

Achieved environmental benefits
The main chemically active constituents contained in the off-gas ($TiCl_4$, Cl_2, CO, and COS) are either absorbed (to form HCl or NaOCl, which are utilised locally or neutralised) or converted to other compounds, such as sulphur (which can be sold) and CO_2 (which is then released to the atmosphere in the main stream of off-gas).

Cross-media effects
Fuel is consumed to keep the oxidiser online during production.

Operational data
The information from one site, relating to emissions of hydrochloric acid and suspended solids to water from the condensation and waste gas scrubbing unit, is given in Section 3.2.3.5.2.

In turn, data relating to varied abatement systems for gases used in the chloride process are given in Table 3.31.

Emissions kg/t	CO incinerator No alkali scrubber	CO incinerator + alkali scrubber	CO incinerator + sulphur recovery
HCl	0.2	0.1	0.05
Cl_2	0.003	0.003	0.003
COS*	0.2	0.2	<<0.003
CO	0.2	0.2	<<1
SO_2	4	0.5	1.8
Costs: EUR/t			
Capital +/-30 %	50	150	140
Treatment	5	20	16
* Based on continuous operation of the plant			
Sites	Rotterdam (NL)	Stalingborough Greatham (UK)	Langebrugge Leverkusen (DE)

Table 3.31: Abatement systems for gases – TiO_2 production by the chloride process [20, CEFIC-TDMA, 2004]

A thermal oxidiser is maintained online whenever production units are operational. Techniques used in scrubbing systems will be dependent upon the local design. Markets for co-products should be established as firmly as possible to ensure their manufacture is worthwhile.

Specific emission figures from one site in Germany (Leverkusen) have been reported [42, UBA-Germany, 2001].

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
Refer to Table 3.31 above.

Driving force for implementation
Minimisation of gaseous emissions from TiO_2 production based on the chloride process.

Example plants
The three European plants of TiO_2 production by the chloride process route mentioned in Table 3.31 above.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [70, Environment Agency, 1999], [26, EIPPCB, 2003], [21, The Council of the EU, 1992].

3.2.4.6 Purification of raw $TiCl_4$ and vanadium oxychloride removal

Description
The liquid raw titanium tetrachloride, separated by condensation, is fed into a distillation unit, where it is put into contact with a reducing agent (oil), in order to convert impurities, such as vanadium oxychloride, to lower valency state compounds, remove them by precipitation and, subsequently, treat them with other waste solid metal chlorides.

In particular, vanadium must be almost completely removed, as even small traces of it in the intermediate purified $TiCl_4$ would finally lead to a yellow colouring of the TiO_2 pigments.

Complexing vanadium oxychloride with oil within the distillation column appears to be the only available option known [20, CEFIC-TDMA, 2004]. Careful selection of the oil is necessary to prevent choking and to minimise the formation of chlorinated hydrocarbons.

A high efficiency specifically designed distillation column is required.

Achieved environmental benefits
Indirect environmental benefits result from the application of this technique, as it is one of key unit operations used in the TiO_2 chloride process, determining the process performance upstream and downstream (as well as the TiO_2 product quality).

Without steady operation of this unit operation, efficient operation of the whole plant would not be achieved.

Cross-media effects
Removed vanadium oxychloride adds to the balance of other waste solid metal chlorides.

Operational data
The usage of the oil to complex the vanadium is given in Section 3.2.3.2.3. No other data submitted.

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
The performance of the chloride process and the quality of the final TiO_2 products.

Example plants
Titanium dioxide plant in Greatham, UK (and the other four European TiO_2 plants based on the chloride process route).

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [48, W. Buchner et al, 1989], [26, EIPPCB, 2003], [85, EIPPCB, 2004-2005].

3.2.4.7 Oxidation

Description
Oxidation is one of the key unit processes applied in the production of TiO_2 by the chloride process route.

There are two environmentally equivalent systems:

- a toluene fired furnace, using injection oxygen and titanium tetrachloride which is also preheated with toluene
- a plasma furnace, with the reactants preheated by gas firing.

This is very specialised equipment requiring tailor made designs, which have not always specifically targeted environmental efficiency. However, a key design criterion is maximising the conversion to TiO_2 with minimum energy input, which is clearly an environmental benefit.

Further advances in the design of this equipment have improved online times and allowed for direct chlorine recycling. As a consequence, both have reduced the environmental burden of the operation. The key factor in reactor design is to develop the units to minimise blockage and thereby enable the replacement of the units to be carried out under a planned maintenance regime. Steady state operation is the best option to minimise losses during subsequent shutdowns.

It should be noted, that hot chlorine-rich gases (containing the suspended TiO_2 particles) leaving the oxidation reactor are passed through a long chain of sections included in the gas recycling loop (gas cooling, the TiO_2 product separation, ore chlorination, solids separation, $TiCl_4$ condensation), the tail off-gases to be finally cleaned in the waste gas treatment section (refer to Section 3.2.4.5), and only then released to the atmosphere.

Achieved environmental benefits
High conversion of the $TiCl_4$ into TiO_2, leading to higher energy efficiency in the process and to reducing the impact of the production of TiO_2 on the environment.

Cross-media effects
Prior to the oxidation, the $TiCl_4$ needs to be preheated. Natural gas or steam are used for this purpose. Relevant SO_2 emission data from one site are given in Section 3.2.3.4.7.

Operational data
For the usage of pure oxygen to oxidise titanium tetrachloride refer to Section 3.2.3.2.4. The usage of toluene is included in the balance of energy (refer to Section 3.2.3.3.1).

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
A very modern and compact plant section, requiring less investment and maintenance cost. A highly material and energy efficient oxidation process, e.g. one based on plasma oxidation technology. A high process efficiency translates to reducing the impact of the plant on the environment.

Example plants
Titanium dioxide plant in Greatham, UK (a plasma reactor).
Titanium dioxide plant in Leverkusen, Germany (a toluene fired furnace).
Titanium dioxide plant in Rotterdam, the Netherlands (a toluene fired furnace).

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [48, W. Buchner et al, 1989], [26, EIPPCB, 2003], [85, EIPPCB, 2004-2005].

3.2.4.8 Cooling and separation

Description
Simple corrosion-resistant coolers are designed to minimise internal scouring abrasion with TiO_2 dust, as well as rock salt or sand used for cleaning to prevent deposits of TiO_2. Gas/solid separation is carried out with reverse pulse bag filters, which minimise undesirable dust carryover to the chlorination reactor. Both the coolers and the filters are supported by an efficient monitoring and maintenance regime. Cooler design has improved over time with modern coolers offering easy access for monitoring and maintenance.

Achieved environmental benefits
Reverse pulse bag filters used for the separation of the TiO_2 minimise dust carry-over, and prevent dust transfer into the chlorination systems, thus minimising downtime.

Cross-media effects
The usage of abrasive solids to scour the primary coolers.

Operational data
No data submitted.

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
The operability of the whole plant and, therefore, the manufacturing cost of TiO_2 production depends on both a high onstream factor of the cooling section and an efficient maintenance regime applied in this section. High efficiency reverse pulse bag filters minimise carryover of the dust to the chlorination reactor.

Example plants
Titanium dioxide plant in Greatham, UK (and the other four European TiO_2 plants based on the chloride process route).

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.9 Direct chlorine recycling process

Description
Direct chlorine recycling is currently used as an alternative to the absorption/desorption system, because it allows for an efficient operation, which in turn saves resources. Also, the need for a large tetrachloride inventory ($TiCl_4$ saturated with gaseous chlorine) is avoided. Steady state operation of chlorination and oxidation in tandem is essential to minimise the environmental impact of a titanium dioxide plant. This requires careful design of the systems with experience used to identify and phase out the weak links in the system to minimise downtime.

Achieved environmental benefits
Phasing out the older chlorine absorption/desorption system in favour of the direct chlorine recycling process, results in the simplification and higher operability of the plant, as well as in lessening the impact of the production on the environment (no tail chlorine gas scrubbing with NaOH solution necessary).

Cross-media effects
No data submitted.

Operational data
No data submitted.

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
Lower inventory of $TiCl_4$ saturated with chlorine.

Example plants
Titanium dioxide plant in Greatham, UK (and the other four European TiO_2 plants based on the chloride process route).

Reference literature
[20, CEFIC-TDMA, 2004], [23, The Council of the EU, 1996], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.10 Abatement systems for gases, solids and liquids

3.2.4.10.1 Abatement systems for gases

Abatement systems for gases in the production of titanium dioxide by the chloride process are described in Sections 3.2.4.1.2, 3.2.4.1.3, 3.2.4.4, 3.2.4.5, and Sections 3.3.3.3.6 and 3.3.4.9 which relate to the finishing operations in the production of titanium dioxide, as these operations are, in principle, the same in both the chloride and sulphate process routes. Refer also to Section 3.2.3.7 (Environmental performance – Greatham Works 2002).

3.2.4.10.2 Abatement systems for solids

Abatement systems for solids in the production of titanium dioxide by the chloride process route are described in Sections 3.2.4.3 and 3.2.4.4. Refer also to Section 3.2.4.10.3 below, and to Section 3.2.3.7.

3.2.4.10.3 Abatement systems for liquids

Description
As a titanium dioxide plant is operated to maximise internal co-neutralisation, one general principle that is applied in the design of a new plant is to arrange for the recycling and co-mixing of acid and alkali streams to minimise the usage of materials. It is an overall requirement to stabilise heavy metal impurities to prevent them contaminating the aqueous environment in particular. All residual acids should be neutralised, the pH being, to a certain extent, dependent on local conditions.

Achieved environmental benefits
Lessening the impact of the production of TiO_2 by the chloride process on the environment.

Cross-media effects
No data submitted.

Operational data
Abatement systems for the main liquid and solid emissions applied in titanium dioxide plants operated by the chloride process route are presented in Table 3.32.

Sites	Rotterdam (NL)	Stallingborough (UK) Langebrugge (DE) Leverkusen (BE)
Treatment pH	4	8
Liquid emissions		
Chloride kg/t TiO_2	30 – 300	3 – 300
Fe kg/t TiO_2	8	0 – 1
Solid emissions		
Waste to land (as wet solids) kg/t TiO_2	100	200 – 1000
Notes: $FeCl_2$ export significantly reduces waste. Neutralisation to pH 4 was allowed and required when the plant was set up due to a restriction on landfill space, but the pH 8 limit will be invoked in 2007. Refer also to data included in Section 3.2.3.7 (Greatham site).		

Table 3.32: Abatement systems – liquid and solid emissions from TiO_2 plants, using the chloride process
[20, CEFIC-TDMA, 2004]

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
Reducing the impact on the environment, among others resulting from the requirements of the TiO_2 Harmonisation Directive [21, The Council of the EU, 1992].

Example plants
All five European plants of TiO_2 production by the chloride process route.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003].

3.2.4.11 Co-products for sale or re-use

Description
Ferrous chloride (see Section 7.4), sulphur, sodium hypochlorite and possibly, hydrochloric acid are potential co-products. Their production depends mainly on local markets. The principle to maximise co-product production and minimise resource consumption is an obvious solution and there are good examples of this in the European TiO_2 industry.

The goal to maximise the conversion of wastes into co-products to suit local demand, typically associated with the selection and development of a new location to enable the maximum use of co-products, is a proven long term strategy applied across the European TiO_2 industry.

Achieved environmental benefits
Minimisation of wastes otherwise released to the environment (refer also to data included in Section 3.2.3.7).

Cross-media effects
Often there are local restrictions on markets but, on the other hand, it is counterproductive to transport low cost co-products long distances.

Operational data
No other data submitted apart from these included in the preceding sections. For information on ferrous chloride refer to Section 7.4.

Applicability
In principle, applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
Reducing the impact on the environment, among others resulting from the requirements of the TiO_2 Harmonisation Directive [21, The Council of the EU, 1992].

Example plants
Titanium dioxide plant in Greatham, UK.

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [90, CEFIC-INCOPA, 2004].

3.2.4.12 Energy usage

Description
For the description of energy usage in the chloride process by site, refer to Section 3.2.3.3.1. Plant design is such as to minimise energy usage. Energy saving in an existing plant is also a matter of management and control. Generally a combination of plant design, operation and management is taken into consideration when determining techniques to minimise energy usage. In particular, for new plants it would also include the supply of its power by a high efficiency combined heat and power (CHP) system [86, The Council of the EU, 2004].

The range of energy usage in 1999 in TiO_2 plants operated by the chloride process route is given in Table 3.33.

Energy	Energy use GJ/tonne TiO_2
Black end	6 – 10 (*)
Finishing	12 – 18
Effluent treatment	1 – 3
Total	17 – 29 (*)
(*) Including an older chlorine recycling system applied in 1999, but not used at the present time.	

Table 3.33: Energy usage in 1999 in TiO_2 plants operated by the chloride process route
[20, CEFIC-TDMA, 2004]

These data were also based on the application of a technique in which extra energy was used for chlorine absorption and desorption (at least 4 GJ/t pigment). This technique, however, is no longer in use in the EU titanium dioxide industry.

Achieved environmental benefits
Energy efficiency in the process is also an indirect measure of the impact of TiO_2 production on the environment. The less energy used for TiO_2 production, the less energy used in primary fuels and, consequently, the less emissions of CO_2, SO_X, and NO_X to the atmosphere related to the generation of energy used in the process.

Cross-media effects
No side effects or disadvantages caused by the implementation of this technique are reported.

Operational data
Refer to Table 3.16 and Table 3.33. Refer also to the information on energy usage at the Titanium dioxide plant in Leverkusen [42, UBA-Germany, 2001].

Even though a new set of data detailing energy usage in 2005 was not made available by the EU TiO_2 industry, given the progress made in energy efficiency, it has been reported that the upper level of overall energy usage for the chloride process is currently in the range of 21 to 23 GJ/t, and on average 17 to 22 GJ/t pigment [85, EIPPCB, 2004-2005] (refer to Table 3.29 below, which illustrates a clear downward trend of energy consumption between 1999 and 2002 in Greatham, UK).

Refer also to [42, UBA-Germany, 2001], where the energy demand in 2001 (average figures) for the chloride process route, illustrative for one plant in Leverkusen, Germany, was estimated at the level of 18.8 GJ/t and from this for TiO_2 manufacture 6.1 GJ/t and for follow-up treatment 12.7 GJ/t pigment.

Applicability
Applicable to all plants producing TiO_2 by the chloride process route.

Economics
No data submitted.

Driving force for implementation
Reduced impact on the environment and decreased manufacturing cost of TiO_2 production.

Example plants
Titanium dioxide plant in Greatham, UK (and the other four European TiO_2 plants based on the chloride process route).

Reference literature
[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [85, EIPPCB, 2004-2005], [86, The Council of the EU, 2004], [25, D.G. Heath, 1996], [24, Tioxide Group Ltd, 1995], [73, G.V. Ellis, 1979].

3.3 Titanium dioxide – the sulphate process

3.3.1 Introduction

Titanium dioxide can be made by one of two basic routes: the chloride process (Section 3.2 above) and the sulphate process (as in this Section 3.3). In both processes, pure titanium dioxide powder is extracted from its mineral feedstock after which it is milled and treated to produce a range of products designed to be suitable for the efficient incorporation into different substrates.

Although applied life cycle assessment techniques (see findings of the LCA study in Section 3.4.5) demonstrated that the current versions of the two processes were environmentally equivalent, the two processes are fundamentally different in most aspects. Therefore, in this document the processes and their emission abatement techniques are treated separately. A comparison of the two processes is included in Section 3.4.

3.3.2 Applied processes and techniques – the sulphate process

The sulphate process, described in this section, uses concentrated sulphuric acid to digest the prepared titanium dioxide ore.

The sulphate route uses low concentration ores such as ilmenite as well as higher concentration synthetic slags – see Table 3.34. The greater presence of iron in ilmenite leads to the cogeneration of a greater amount of iron sulphate from the process. A minimum quantity of iron is required to ensure a high conversion efficiency, thus 80 % TiO_2 is the highest concentration that can be used without unacceptable losses. Only the sulphate process can readily form both crystalline forms (anatase and rutile) of TiO_2.

Type of feedstock	Component	Portion (mass content in %)
Ilmenite	TiO_2	44 – 61
Slag	TiO_2	75 – 80

Table 3.34: Components in main mineral feedstock – TiO_2 production, the sulphate process [20, CEFIC-TDMA, 2004]

As illustrated in Figure 3.4 below, the sulphate process generally consists of the following sequential stages.

3.3.2.1 Raw material import and preparation

Ore containing titanium dioxide is usually sourced from outside Europe, however, there is a source of rock ilmenite in Norway, which is used by some companies.

Feedstock purchasing decisions are multidimensional (economic, plant operability, product quality, cost of abatement, waste disposal, etc.) and can change over time. The feedstock of the required purity is purchased according to a set of specifications, set as part of the feedstock purchasing strategy. One of the critical factors is the question of impurities and, therefore, the purity check of titanium ore plays an important role in the production process.

There are two main issues here. Some heavy metal impurities are not acceptable since trace levels in the final product can influence the whiteness and brightness. The other is trace levels of Naturally Occurring Radioactive Materials (NORM) which are present in some ores. This means that with these feedstocks, the processing is subject to the Directive, 96/29 [22, Euratom, 1996], which may mean that the ore handling and disposal of some wastes is subject to exposure assessment. The companies take all the necessary precautions to protect personnel and the environment as required by Euratom.

The raw ore is usually stored in covered storage silos. Although covered storage is, in principle, not necessary for the sulphate process, it does have advantages. If the ore becomes wet in transit then it must be dried before further processing. It is then ground using large ball mills to produce optimum size particles (typically 40 – 60 µm) for efficient dissolution with concentrated sulphuric acid. The main environmental issue at this stage is dust emissions, which are normally controlled by operating the milling and conveying equipment under mild suction and discharging the gas through bag filters. The content of combustion gas is monitored when drying is required. The collected ore dust is conveyed to a storage bin for the milled ore.

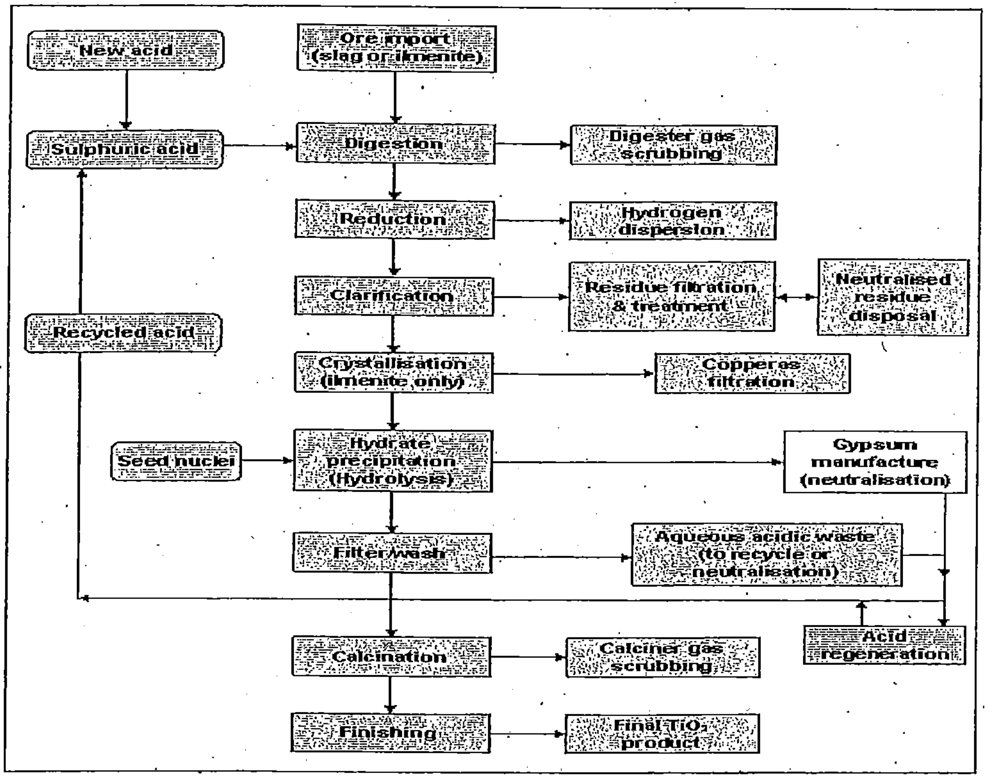


Figure 3.4: Outline flow diagram – titanium dioxide production by the sulphate process [20, CEFIC-TDMA, 2004]

3.3.2.2 Digestion

Digestion of the ore can be operated either batch wise or continuously. The more usual process is batch. It is noted that batch processing is preferred by the EU producers. The continuous process has been tried in the past, however with some feedstock types, this process works with lower efficiency (see Section 9.3.2.1). Since the EU producers have an extensive experience and the necessary know-how to run the batch process optimally, all European sites use the batch process. The ilmenite or slag (or a carefully controlled blend of both) is mixed with highly concentrated sulphuric acid (80 – 95 %) and this is necessary to digest the feedstock containing TiO_2. A highly exothermic reaction is initiated by the addition of a measured quantity of steam, water or diluted acid and takes place at around 140 °C.

The equation for the digestion reaction may be summarised as:

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

During the batch process, the exothermic reaction raises the temperature of the reactor from 180 to 210 °C and water evaporates. Agitation/mixing of the reactor is achieved by air blowing. In the case of ilmenite as a feedstock, the off-gases contain small quantities of dust, sulphur dioxide and acid fumes, which are removed by scrubbing. Using slag, the off-gases contain dust, sulphur dioxide, sulphur trioxide and traces of hydrogen sulphide, which are normally removed by a multistage scrubbing system.

Two sites use a blend of slag and ilmenite and treat off-gases by normal scrubbing, although using a multistage scrubbing system is a possible option.

In most cases, the scrubbing systems have been uprated in the recent past as a result of the Titanium Dioxide Harmonisation Directive [21, The Council of the EU, 1992]. The systems are usually custom built to suit local conditions. The cyclic nature of the batch process requires that the scrubbers have to be capable of handling large volumes of gases during the short reaction period (minutes) followed by relatively low volumes during the subsequent long 'bake' period (hours).

The resulting solid cake is dissolved in water and acid recycled from a subsequent washing step. Any insoluble material is removed by flocculation and filtration. Afterwards, the titanyl sulphate ($TiOSO_4$) in the clarified liquor is hydrolysed which results in a precipitation of the hydrated TiO_2, while other sulphates, e.g. iron-sulphate ($FeSO_4$), remain in the solution.

Because of the exothermic reaction, the quality and reactivity of the ore has to be checked carefully. Normally the amounts of all components, i.e. ore, concentrated acid and in the case of slag, oleum are carefully metered before they are added to the reactor in order to prevent unintentional pressure release.

The primary intermediate from the reaction is titanyl sulphate ($TiOSO_4$) and both ferrous and ferric sulphates are produced as by-products, all of which are held in solution in a supersaturated state and care must be taken to avoid instability of the liquor to prevent uncontrolled precipitation of the TiO_2 crystallites.

Off-gases are treated by a variety of methods most of which are dependent on local conditions (refer to Section 3.3.4.10.1).

3.3.2.3 Reduction

When the primary ore is ilmenite (or a blend of slag with ilmenite) the digester liquor is contacted with scrap iron to convert ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}), otherwise the iron would remain with the TiO_2 throughout all subsequent processing stages. The quality of the scrap iron has to be controlled in order to prevent the contamination of the solution with heavy metals like chromium or nickel. This process generates a small amount of hydrogen, which is normally rendered harmless by dispersion in air.

The explosion risk is extremely low particularly when the area is designated free from ignition sources. It should be noted that the sulphate process is not subject to the Seveso II regulations [23, The Council of the EU, 1996].

One site blends liquor from slag digestion with unreduced liquor of ilmenite digestion and thus uses no scrap iron.

3.3.2.4 Clarification and crystallisation

Any suspended material is removed from the solution by flocculation and filtration. It is washed with dilute waste acid to recover the titanyl sulphate. The acidic filtrate liquors are recycled back to the process. The solid residue is neutralised with lime or limestone before going to landfill. This material can sometimes be used as an inert filler or in other applications after further treatment but this is usually not possible due to the limited markets and the presence of impurities, which originate from some ores.

At one site, a small part (<3 %) of the residues is neutralised with caustic soda, washed, dried and added in the digestion step to enhance the yield of TiO_2.

When ilmenite (or a blend of slag with ilmenite) is the main feedstock, the clarified solution is usually pumped to batch cooler/crystallisers to remove the bulk of the iron sulphate as the solid heptahydrate ('copperas'). This solid and its associated products are widely used for example in water treatment, pharmaceutical and pigment industries. Reference is made here to Section 7.5 on 'Copperas and related products'. The iron-depleted product liquor is polished using filters to remove fine particles and is finally concentrated in evaporators.

3.3.2.5 Hydrolysis (hydrate precipitation)

Hydrated titanium dioxide is produced by hydrolysing the liquor with steam in rubber and brick-lined mild steel vessels.

The hydrolysis reaction is:

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

Precipitation of the hydrated TiO_2 is achieved by boiling the liquor for some hours followed by cooling to 60 °C. The addition of the correct TiO_2 nuclei to the batch determines the final crystal size and form of the titanium dioxide (anatase or rutile crystals). It is noted that there are many local variations of this stage of the process.

The hydrated TiO_2 is filtered off from the suspension and the filter cake is washed to remove any absorbed metal ions. At this stage of the process, the spent acid with a concentration of 20 - 25 % H_2SO_4 and 10 – 15 % of soluble salts (mainly iron, aluminum and magnesium sulphates) arises and is either recycled or neutralised with lime/limestone to produce gypsum which is preferentially sold at local markets as a commercial product (e.g. white gypsum) or, if there is no possibility to sell it, it is landfilled.

It should be noted that because the main process liquor is a supersaturated solution of hydrated titanium ions, it has to be treated carefully to prevent uncontrolled hydrolysis ('instability'). To reflect this, the process requires steady state operations both in production rate and temperature control. Liquor, especially that made from ilmenite, is often preconcentrated to aid stability and to help control hydrolysis.

Working with so-called low 'F/T' (iron/titanium) ratios is an example of the expertise that has been built up in the industry over the years. All systems, as long as they allow good control during precipitation, appear to be equivalent from the operational point of view. The unique variable is the size of the flocculates of crystallites. This is carefully controlled to allow for as narrow as possible, consistent particle size distribution of calciner discharge downstream in the process.

3.3.2.6 Filtration and washing

The precipitated hydrated TiO_2 is separated on vacuum filters from the mother liquor (i.e. 'strong' acid, approx. 20 – 25 % H_2SO_4). This acidic filtrate can either be reconcentrated and recycled back to the digestion step or may be neutralised with lime/limestone and the product gypsum sold for wallboard manufacture, etc. After the separation of the mother liquor, the filter cake is washed with water or a weak acid. The resultant solid is slurried with dilute sulphuric acid and aluminium or a solution of trivalent titanium is usually added as a reducing agent to maintain the iron in the ferrous state.

The slurry is 'leached' (sometimes called 'bleaching') at 50 °C to remove final traces of iron. Thus the residual solid metals (Fe, Cr, Mn, and V) are eliminated from the hydrate by the addition of a reducer additive (e.g. trivalent titanium or aluminium) and acid (leaching agent). The use of zinc is not recommended due to its potential effect in the food chain.

The slurry then undergoes final washing and dewatering. The pulp still contains adsorbed sulphuric acid, which is impossible to remove by washing. Conditioning agents and rutile nuclei can be added at this stage to the resulting pulp to enhance crystallite growth and to determine the final crystal form during calcination.

One site in the EU-25 reports the usage of concentrated sulphuric acid for bleaching, but there are no details of this technique available [85, EIPPCB, 2004-2005].

3.3.2.7 Calcination

The rotary kilns are directly fired with oil or gas. The pulp moves under gravity countercurrently to the combustion gases. Water and oxides of sulphur are driven off the pulp. Temperature control (particularly where there is direct contact with the gas flame) is important in the production of the correct crystalline type and particle size of the pigment..

As with digester gas, scrubbing calciner gas treatment has been upgraded in the past in order to reduce SO_2 emissions to below the limit prescribed in the Titanium Dioxide Harmonisation Directive [21, The Council of the EU, 1992]. TiO_2 dust is removed by scrubbing and recycled. SO_3 is removed by electrostatic precipitators. The SO_2 component of the gas is either scrubbed out or catalytically oxidised to SO_3 and absorbed to form sulphuric acid, which in turn is recycled. In one site, the off-gases are partly used for the preconcentration of waste acid.

3.3.2.8 Effluent treatment

It is common practice in the titanium industry to use the terms 'strong' and 'weak' acid. They are defined in the TiO_2 Harmonisation Directive [21, The Council of the EU, 1992]. In simple terms, strong acid is sulphuric acid at the strength it occurs immediately after hydrolysis of the digestion cake (see Section 3.3.2.2 above). Weak acid is the sulphuric acid that results from the dilution of the strong acid particularly when washing the precipitated TiO_2 pulp that results from the digestion cake hydrolysis. There are two options for the treatment of the strong waste acid: reconcentration followed by recycling, or neutralisation – see Section 3.3.2.6 and Figure 3.5. Weak waste acid is directly recycled (there is only a limited capacity for this within the process) or neutralised. It is not cost effective or environmentally sensible to reconcentrate weak acid.

3.3.2.9 Finishing section

The finishing section is common to the chloride and the sulphate processes. The resulting solid is cooled, milled, coated, washed, dried, micronised and packed. Before coating, two stages of milling are used:

- dry milling to break down aggregated particles from the calcining process (up to 20 mm) to 75 - 100 µm; and
- wet milling to achieve fine particles of the correct size for optimum pigment properties (0.2 - 0.4 µm).

3.3.2.9.1 Coating

The main purpose of coating is to improve durability and to lessen the yellowing which occurs in certain types of paints, and also to improve the dispersibility of the pigments within their particular substrates.

Coating involves the deposition of a small percentage of other materials on to the pigment surface. Hydroxides of silica, titanium, zirconium and aluminium are commonly used. The coating agents are normally added to the milled slurry as soluble sulphates or chlorides, while it is continuously stirred.

By adjusting the solution pH, hydrated oxide is precipitated on to the surface of the pigment particles. Coatings of two or more hydrated oxides may be applied to a pigment, either separately by successive operations or simultaneously in one operation.

3.3.2.9.2 Final processing

After coating, the pigment is washed and dried before being ground by entrainment in high velocity steam in a microniser or fluid energy mill to separate the aggregated particles. This stage is essential in order to produce the high quality required for all modern pigment applications.

Particulate matter generated during micronising is removed to low levels by bag filters prior to the condensation of steam from fluid energy milling, either in conventional heat exchangers or in a barometric leg. In case steam condensation is not used, particulate matter is removed prior to steam venting to the atmosphere.

Many TiO_2 pigments are also given a light organic surface treatment to improve their dispersibility in a variety of media. This is usually carried out during the final milling stage. A variety of organic compounds are used as additives. The most common types are polyols, amines and silicone derivatives.

The final product is packed in paper sacks (either manually or automatically); packed in 'semi-bulk' containers; or exported in road tankers.

3.3.2.10 Abatement systems for aqueous emissions from the sulphate process

If there were no effluent treatment operations then the sulphate process would produce large quantities of strong waste sulphuric acid and aqueous acidic effluents, which contain metal sulphates and waters from the post-treatment section.

The two main systems used to treat this strong waste acid are acid recycling or neutralisation. However, it must be understood that in modern titanium dioxide manufacturing processes there is often a whole co-product strategy including the production and marketing of copperas, which influences the particular combination of treatments that is chosen for any particular site – refer to Section 7.5.

3.3.2.10.1 Acid recycling

The strong waste acid is concentrated by evaporation in a complex multistage process to approximately 70 % H_2SO_4. During the concentration process, the soluble salts are precipitated and are filtered off after the cooling of the 70 % acid. This acid can be used again in the digestion step or can be further concentrated up to approximately 80 % H_2SO_4, and then used in the digestion of the ore containing TiO_2.

One site reports that the waste acid, after being concentrated to an appropriate level, is used for the production of phosphoric acid, the latter being used for the production of fertilisers.

The separated filter-salts (mainly iron sulphate in the monohydrate form) can be thermally decomposed to iron oxide and sulphur dioxide, which is converted to fresh sulphuric acid, which is used in the digestion step, too. So there are essentially two recycling loops: one dealing with the acid that remains an acid in the TiO_2 process, and one dealing with the acid which is transformed into a metal sulphate and needs to be decomposed to recover the sulphur values. Alternatively the filter salts can be neutralised for use in the fertiliser industry or for landfill.

The production of sulphuric acid from the SO_2 of filter salts roasting is the point at which the operation is covered by the sulphuric acid process – see BREF on LVIC-AAF.

The overall scheme is shown in Figure 3.5 below.

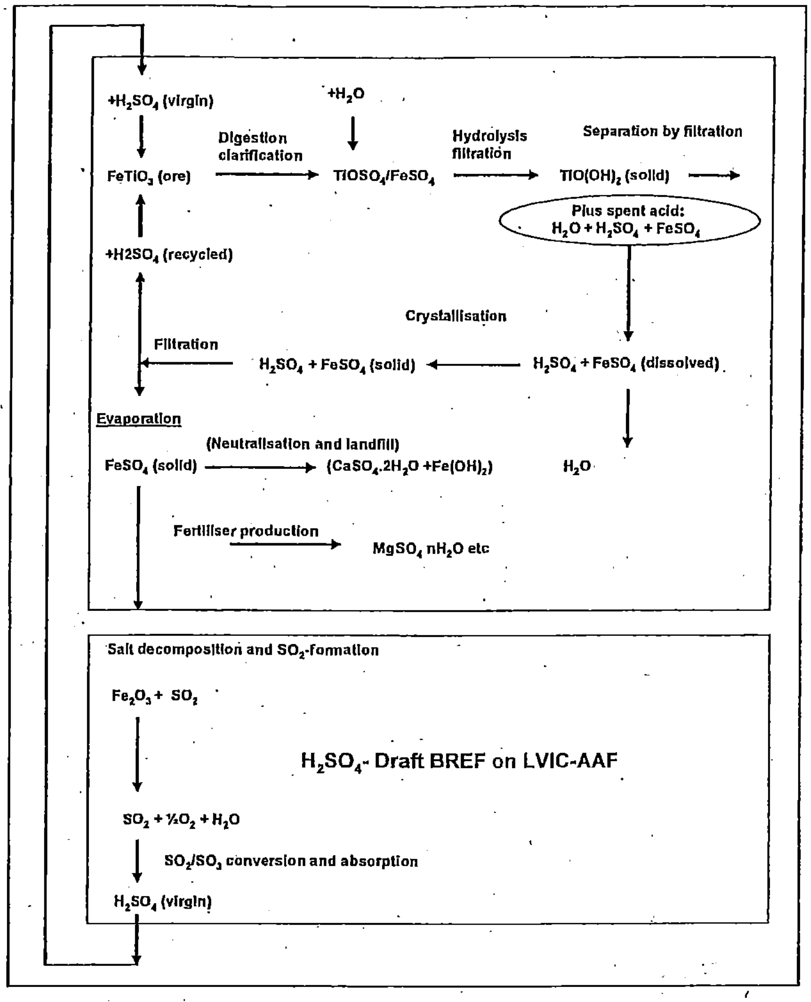


Figure 3.5: Overall process-scheme of sulphuric acid recycling – TiO_2 sulphate route [20, CEFIC-TDMA, 2004]

3.3.2.10.2 Neutralisation

Neutralisation is used for both strong and weak acid. The process normally adopted for strong acid is a two-stage neutralisation:

- stage 1: Neutralisation with chalk or limestone in which pure white gypsum is produced
- stage 2: Neutralisation to pH 8 – 9 with lime to produce 'red gypsum', which is a mixture of stabilised metal hydroxides and gypsum.

The purpose of this staged process is that it is designed to produce marketable co-products for use in many industrial and agricultural applications. If white gypsum is required for plasterboard then extra process steps are required to ensure the gypsum's properties are compatible with the plasterboard manufacturing requirements. The long term strategy of the TiO_2 sulphate process industry is aimed at the optimum balancing of inputs and outputs, the best example here being probably white gypsum, which – because of its good quality – finds its applications in the production of gypsum plasterboards, even though there are abundant supplies of cheap, subsidised flue-gas desulphurisation (FGD) gypsum across Europe.

Weak acid is usually also neutralised by a two-step process using limestone and lime producing single product ('red') gypsum.

3.3.2.10.3 Waste water from post treatment

Waste water contains mainly pigment and sodium sulphate, which results from using caustic and caustic based additions in the final coating process. Depending on the quality, it can either be sent to the rivers after removing of the suspended solids, or treated and then combined with the acidic waste water from the sulphate plant.

3.3.2.10.4 Cooling waters

Any water that is used specifically for cooling can be considered using the horizontal 'Industrial Cooling Systems' BREF.

3.3.2.10.5 Co-products

The principle co-products and their uses are listed below:

- ferrous sulphate is used in municipal waste water treatments (phosphorus removal), as raw material for iron oxide pigments and as an additive for concrete (Cr anti allergen), fodder and fertilisers
- ferrous sulphate is converted to ferric form, which is used in water treatment
- white gypsum (for wallboards and the cement industry) and red gypsum (agricultural use). Red-gypsum can also be used as a solidifying agent for loose clay soils to make them stable (for highways, etc). Red gypsum, blended with organic fertiliser, is also used for capping and landscaping activities of quarries, landfills and contaminated sites. Finally, this co-product can be used in the cement industry
- ilmenite residue (ilmenite sand) can be used as a silicate product in the cement industry and as a filler in land improvements
- iron oxide from filter salt roasting is used in the cement industry
- concentrated acid can be used in the fertiliser industry
- a high quality CO_2 may be produced during gypsum manufacture. This may be bottled and sold for carbonated drinks.

3.3.3 Present consumption and emission levels – the sulphate process

All data originate from the European sites designated in Table 3.5 (apart from Police, Poland and Celje, Slovenia) and are for the year 1999 [20, CEFIC-TDMA, 2004] and, unless stated otherwise, all consumption and emission units are in kg per tonne of TiO_2 pigment. For current environmental performance of the TiO_2 production using sulphate process – see Figure 3.4 and refer to the environmental performance case study in Section 3.3.3.6.

3.3.3.1 Raw materials consumption

3.3.3.1.1 Digestion

Ore usage

The TiO_2 content of the main feedstock range from 44 to 80 % and most sites have their unique range of feedstock which best suit their supply and processing conditions. Usually in any one period, a site will use either slag or ilmenite, but blends of slag and ilmenite can also be used and two sites use them to good effect.

It is noted that the impact of different ores is a complex process, for example, the use of slag increases the overall energy consumption but reduces the solid emissions, however, with an active co-product sales policy this effect can be balanced. This is covered in detail in the life cycle assessment in Section 3.4.5.

Main materials into section	Ilmenite	Slag	TiO_2 throughput
kg/t TiO_2 (average)	1662	956	1131
kg/t TiO_2 (maxima of averages)	2540	1405	1222
kg/t TiO_2 (minima of averages)	220[(1), (2)]	0	1057

Notes:
1. This figure is much below theoretical consumption, but it is incorrect to imply that the site using the minimum amount of ilmenite also used the minimum amount of slag;
2. In this case, one site blended a small amount of ilmenite with the main slag feed in 1999.

Table 3.35: Usage of the main titaniferous raw materials in the sulphate process

The usage of the main titaniferous raw materials in the sulphate process is given in Table 3.35. As with the chloride process, this makes direct comparison of usages not very meaningful. Looking at the TiO_2 throughput can provide a more useful comparison. It is seen that the average consumption is 1131 kg TiO_2 in the feedstock per tonne of TiO_2 pigment with a range of +/- 8 %. It is considered that a variation across this range is not very significant, particularly in the light of the variation in the feedstock blends.

Sulphuric acid usage

The consumption of sulphuric acid is primarily dependent upon the impurity content of the feedstock, however, it is also influenced by the choice of effluent treatment, which controls how much recycled acid can be used. This is a complex environmental issue and it contributes to the life cycle assessment balance because there is an interplay of different environmental effects depending on the acid and ore combination that is used. Sulphuric acid usage in titanium dioxide production by the sulphate process is given in Table 3.36.

Main materials into section	Sulphuric acid new (as 100 %)	Sulphuric acid recycled (as 100 %)	Sulphuric acid total (as 100 %)
kg per t TiO_2 (average)	2362	1067	3250
kg per t TiO_2 (maxima of averages)	3740	1634	4394
kg per t TiO_2 (minima of averages)	956	80	2430

Table 3.36: Sulphuric acid usage in titanium dioxide production by the sulphate process

3.3.3.1.2 Reduction

Scrap iron is required if ilmenite or a blend of slag and ilmenite is the feedstock. The usage is primarily dependent on the amount of ferric iron in the system. Scrap iron usage is given in Table 3.37.

Main materials into section	Scrap iron
kg per t TiO_2 average	150
kg per t TiO_2 max	250
kg per t TiO_2 min	127

Table 3.37: Scrap iron usage

3.3.3.1.3 Clarification and crystallisation

Small amounts of filter aid are used to assist the removal of unreacted fine particles of impurity from the liquor. No other materials are consumed at this stage of the process. However, the residue is neutralised to stabilise metal ion impurities and remove any retained acid before subsequent use or disposal. Lime or limestone is normally used for this purpose. These data are included in the table of general materials usage (Table 3.38) given below.

3.3.3.1.4 Hydrolysis, filtration and washing

No significant materials are consumed during these stages of the process, however it is here that the strong waste acid is produced which requires treatment. This is done by reconcentration, etc. or by neutralisation as described above in Section 3.3.2.10 and illustrated in Figure 3.5.

3.3.3.1.5 Calcination

Small proportions of mineral salts, such as KCl, are added to assist crystal growth.

3.3.3.1.6 Effluent treatment

See Sections 3.3.3.1.8 and 3.3.3.1.9 below.

3.3.3.1.7 Finishing

Inorganic metal sulphates and caustic soda are consumed at this stage and their usage is included in the summary Table 3.38 below.

3.3.3.1.8 Abatement systems for aqueous emissions from the sulphate process

Significant quantities of lime and limestone are used if neutralisation is the chosen abatement system – see Table 3.38, covering also the usage of materials in the finishing section.

Main materials into section	$Al_2(SO_4)_2$ (100 %)	H_2O_2 (50 %)	$Ca(OH)_2$ (100 %)	$CaCl_2$ (100 %)	$CaCO_3$ (100 %)	NaOH (100 %)	$Al(OH)_3$ (100 %)
kg per t TiO_2 (average)	21	12	363	15	1380	90	30
kg per t TiO_2 (max. average)	21	12	800	15	2954	168	53
kg per t TiO_2 (min. average)	21	12	30	15	36	46	15

Table 3.38: Materials used – abatement systems aqueous emissions and the finishing section [20, CEFIC-TDMA, 2004]