

3.3.3.1.9 Abatement systems for gaseous emissions from the sulphate process

Small amounts of caustic and peroxide may be used. These are included in Table 3.38 above.

The main point to note when summing up the major materials used in the whole process (not included in the boxes and tables above) is the wide range of neutralising materials that are used depending whether or not neutralisation is the main method of effluent treatment. Some of the data are specific for one or two sites. It should be pointed out that the more internal recycling that is done, the less neutralising raw materials are used.

3.3.3.2 Utilities consumption – energy and water

The original concept was to give energy and water consumptions for each process stage as is done above, however this was found to be excessively complicated due to limitations on the measurement systems that the sites have in place and in the case of water, the many recycling arrangements that exist. Instead, a simplified set of data for the sites as a whole is given.

3.3.3.2.1 Energy

The overall energy consumption for the production of a titanium dioxide pigment based on the sulphate process is in the range of 24 to 45 GJ/t, with an average of approximately 36 GJ/t.

Energy units are GJ per tonne of TiO₂ pigment. Consumptions of electricity, steam, gas and heavy fuel oil, given in Table 3.39, are for the following three major sections of the process [20, CEFIC-TDMA, 2004]:

1. Ore preparation to calcination – Sections 3.3.2.1 to 3.3.2.7.
2. Finishing – Section 3.3.2.9.
3. Effluent treatment – Section 3.3.2.8.

| Process section | Sulphate average | Maximum sulphate | Minimum sulphate |
|--|------------------|------------------|------------------|
| Date | 1999 | 1999 | 1999 |
| Energy TiO₂ usage ore preparation to calcination/oxidation | | | |
| Electricity GJ/t | 1.9 | 3.1 | 1.0 |
| Steam GJ/t | 5.5 | 9.0 | 1.4 |
| Gas GJ/t | 9.7 | 12.5 | 7.3 |
| Energy: TiO₂ usage finishing | | | |
| Electricity GJ/t | 1.3 | 3.4 | 0.6 |
| Steam GJ/t | 8.5 | 12.8 | 1.2 |
| Gas GJ/t | 2.4 | 4.2 | 0.0 |
| Energy effluent treatment | | | |
| Electricity GJ/t | 1.0 | 2.5 | 0.1 |
| Steam GJ/t | 3.3 | 11.4 | 0.0 |
| Gas GJ/t | 0.4 | 3.0 | 0.0 |
| Heavy fuel oil, coal, coke GJ/t | 2.4 | 8.7 | 0.0 |
| Overall total energy per site | 36.4 | 45.3 | 23.7 |

Table 3.39: Energy consumption in TiO₂ production – the sulphate process [20, CEFIC-TDMA, 2004]

It should be noted that these data rows are the average, maxima and minima of all the data for the individual sections of the individual sites [20, CEFIC-TDMA, 2004]. As with the chloride process, the energy usage analysis has been simplified [20, CEFIC-TDMA, 2004].

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It should be also noted that these are site usages of energy and do not include energy used in the production of raw materials (ore, oxygen, etc). These are taken into account in the LCA study - refer to Section 3.4.5. Also the LCA has a recognised and auditable method of using realistic heat/power energy conversion efficiencies [20, CEFIC-TDMA, 2004].

Ore preparation to calcination – comments

A number of sites have a significantly lower energy consumption in this section of the process than all the others for no simple reason. There is a variation about the mean of approximately +/-30 %. Typical explanations are given below:

- electricity usage largely depends on the number and size of streams
- drying feedstock uses up to 0.5 GJ/t of titanium dioxide pigment
- slag will require more energy for milling, i.e. about 0.2 GJ/t
- steam: slag plants need not use concentrators worth ~ 0.5 – 1.3 GJ/t
- use of ammonia for crystallisation cooling can reduce energy consumption
- steam usage at concentration can vary widely with the use or not of liquor preheaters and multi-effect concentrators
- gas is mainly used for calcination and its usage depends on the type of dewatering (feed solids), type of feed and the use of hot gas recycling. Pressure filters on calciner feed can save 2 – 3 GJ/t TiO₂, while the recycling of hot gases during calcinations saves ~ 0.5 GJ/t TiO₂.

Typical values are:

- rotary vacuum screw no hot gas recycling (38 % solids): 12.5 GJ/t
- pressure filter screw + hot gas recycling (45 % solids): 7 – 8 GJ/t
- it is common to have any combination in between.

Acid recycling with roasting all the salts adds approximately an extra 11.5 GJ/tonne to the total compared with neutralisation – see box in 'Effluent treatment – comments' section below:

Finishing – comments

Variations here are easier to account for since the dominant energy (steam) consumer is the final fluid energy milling ('micronising'). The higher quality pigment grades often require two passes of milling, i.e. using almost twice the energy as single milled grades. Each company will have its own range of the double milled grades, which is dependent on its customer base. One site does not micronise at all. Other variations are:

- electricity usage varies with the techniques for dry and wet milling (Raymond mills, sand mills, beads), as well as with the production of uncoated grades. Wet milling can add ~ 1 GJ/t TiO₂ pigment produced
- gas is normally only used for drying. The differences can be explained by technology (a spray dryer only uses gas, a band dryer uses different combinations of gas and steam)
- steam is used for milling and drying. Milling usage, depending on the type of grades, can vary from 5 to 10 GJ/t, and average about 7 GJ/t. Double micronising can add up to ~ 5GJ/t TiO₂ pigment.

Effluent treatment – comments

Neutralisation requires significantly less primary energy than acid recycling. This is because for recycling both reconcentration of the 'strong acid' and roasting of the filter salts are usually required to bring the acid to the required strength. In Europe, many different permutations are adopted which means that the contribution to the overall energy usage varies significantly from plant to plant (see Section 3.3.3.2.1 above) as detailed below:

- one site recycles and neutralises, and some of the salts are exported for roasting
- another site exports its strong acid to another site for reconcentration and subsequently reimports an equivalent quantity of the reconcentrated acid
- another site recycles and neutralises its filter salts
- some sites neutralise only
- one site exports its filter salts to another for roasting and reimports an equivalent quantity of acid
- three sites recycle acid and roast salts. The energy usage needed for roasting all salts adds to ~ 5 GJ/t TiO₂.

As seen in Table 3.40, in broad terms, neutralisation uses 2 – 3 GJ/t of site energy whereas acid recycling (with roasting all the salts) adds approximately 14 GJ/t, the difference being as high as up to 12 GJ per tonne of TiO₂ pigment produced:

| | |
|--|------|
| Average energy usage for neutralisation GJ/t | 2.3 |
| Maximum energy usage for neutralisation GJ/t | 6.5 |
| Minimum energy usage for neutralisation GJ/t | 0.2 |
| Average energy usage for acid recycling GJ/t | 13.8 |
| Maximum energy usage for acid recycling GJ/t | 18.0 |
| Minimum energy usage for acid recycling GJ/t | 10.2 |

Table 3.40: Energy usage in the production of TiO₂ via the sulphate process

3.3.3.2.2 Water consumption

Because of different technological options used, water consumption is specific to each site. Water saving in an existing plant is often a matter of management and control. This is particularly the case on the older sites when, in former times, water was freely available and not seen as a commodity that was worth saving. Awareness of the main users is an essential feature. Modern sulphate plants are generally fitted with equipment that is designed to be water efficient, and there are many ways that water can be re-used in the sulphate process.

| Site/process type | Averages sulphate | Maximum sulphate | Minimum sulphate |
|--|-------------------|------------------|------------------|
| Date | 1999 | 1999 | 1999 |
| Total water per site m ³ /t | 189 | 770 | 60 |
| Industrial total m ³ /t * | 77 | 210 | 35 |
| Sea or river water m ³ /t | 246 | 720 | 79 |
| * 'Industrial total' is water imported into site for TiO ₂ processing and effluent treatment, except for cooling water for once through open systems, denoted here as sea or river water. | | | |

Table 3.41: Water consumption in the production of TiO₂ via the sulphate process

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3.3.3.3 Emissions to air

In contrast to the chloride process, plant sections are not usually integrated as far as gaseous emissions are concerned, so it is easier to attribute specific emissions to particular sections of the plant.

3.3.3.3.1 Raw material import and preparation

The major concern here is dust. Some sites monitor their emissions from their feedstock dryers; often these are not regarded as significant. Dust and NO_x emissions are given in Table 3.42.

| Emitted substance | Dust | NO _x |
|-------------------------------------|-------------------|-----------------|
| Typical treatment method | Bag filters | |
| kg per t TiO ₂ (average) | 0.04 | 0.03 |
| kg per t TiO ₂ (max) | 0.08 | 0.04 |
| kg per t TiO ₂ (min) | 0.0002 | 0.002 |
| Collection period | 1999 | 1999 |
| No of data (average) | 11 | 3 |
| Typical volume based value | Dust | NO _x |
| mg/Nm ³ (average) | 39 ^(*) | 23 |

* If one site is excluded, the average would be 18 mg/Nm³.

Table 3.42: Dust and NO_x emissions – TiO₂ production, the sulphate process [20, CEFIC-TDMA, 2004], [85, EIPPCB, 2004-2005]

3.3.3.3.2 Digestion

SO₂ and H₂S emissions from the digestion section for treatment are given in Table 3.43.

| Gaseous emissions for treatment | | |
|---|-----------------|------------------|
| Emitted substance | SO ₂ | H ₂ S |
| Typical treatment method | Scrubbing | Scrubbing |
| kg per tonne TiO ₂ (average) | 0.47 | 0.003 |
| kg per t TiO ₂ (max) | 1.91 | 0.010 |
| kg per t TiO ₂ (min) | 0.00 | 0.000 |
| Collection period | 1999 | 1999 |
| No of data (average) | 3 | 3 |
| No of data (max.) | 10 | 4 |
| No of data (min) | 1 | 1 |
| Typical volume based value | SO ₂ | H ₂ S |
| mg/Nm ³ (average) | 87 | 4 |

Table 3.43: Gaseous emissions in the digestion section – TiO₂ production, the sulphate process [20, CEFIC-TDMA, 2004]

Sulphur dioxide emissions are usually the main concern here. It is noted that if the feedstock is rock ilmenite then the SO₂ emission is likely to be zero and, in this case, simple water scrubbing can be used to remove any acid mist and SO₃. If slag is the feedstock, then small amounts of H₂S are emitted. Water and caustic scrubbing can be used.

3.3.3.3.3 Reduction

Some hydrogen is emitted in the reduction step – see Table 3.44.

| Emitted substance | Hydrogen |
|---|----------|
| Typical treatment method | None |
| kg per t TiO ₂ (average) | 1 |
| kg per t TiO ₂ (max) | 2 |
| kg per t TiO ₂ (min) | 0 |
| Collection period | 1999 |
| Data estimated at one site only, no volume based data available | |

Table 3.44: Hydrogen emissions during the reduction step

3.3.3.3.4 Hydrolysis, filtration and washing

There are no atmospheric emissions from these sections, however reference can be made to Section 7.5 on 'Copperas and related products', since some atmospheric emissions occur depending on how the copperas is subsequently treated to convert it into saleable co-products.

3.3.3.3.5 Calcination

As can be seen from Table 3.45, sulphur dioxide emission is the major concern for all countries of the European Union. The Czech plant did not have its sulphuric acid plant operational until the 4th quarter of 1999, hence the average for the year is high. Most plants have proprietary equipment in which there is the catalytic conversion of SO₂ to SO₃ and subsequent absorption to sulphuric acid, which is recycled. The performance of these units is dependent on many factors such as age of catalyst, degree of dust contamination, size and number of units, etc. (refer to the BREF on LVIC-AAF).

The explanation of the large range of data numbers is that some sites have 'continuous' measurement. One plant has a unique arrangement where the calciner gases are fed directly to their sulphuric acid plant. Another has a direct water scrubbing system that is 'waste-free' since all the scrubbing water is re-used in the process.

| Emitted substance | Acid mist | Dust | SO ₂ | NO ₂ |
|-------------------------------------|----------------------------------|---------|---------------------|-----------------|
| Typical treatment method | Electrostatic mist precipitators | | Catalytic oxidation | None |
| kg per t TiO ₂ (average) | 0.65 | 0.24 | 3.5 | 0.6 |
| kg per t TiO ₂ (max) | 1.57 | 0.65 | 12.10 | 1.20 |
| kg per t TiO ₂ (min) | 0.00 | 0.00 | 0.01 | 0.04 |
| Collection period | 1999 | 1999(*) | 1999 | 1999 |
| No of data (average) | 4 | 4 | 70082 | 2 |
| No of data (max) | 4 | 10 | 175200 | 4 |
| No of data (min) | 4 | 1 | 4 | 1 |
| Typical volume based value | | | | |
| mg/Nm ³ (average) | 33 | 23 | 713 | 98 |
| (*) Four sites – estimated data | | | | |

Table 3.45: Gaseous emissions from calcination – TiO₂ production, the sulphate process [20, CEFIC-TDMA, 2004]

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3.3.3.3.6 Finishing

Dust emissions from the finishing section are given in Table 3.46.

| Emitted substance | Dust from milling | Dust from micronising |
|-------------------------------------|----------------------|-----------------------|
| Typical treatment method | Cyclones/bag filters | Bag filters |
| kg per t TiO ₂ (average) | 0.01 | 0.156 |
| kg per t TiO ₂ (max) | 0.02 | 0.370 |
| kg per t TiO ₂ (min) | 0.00 | 0.002 |
| Collection period | 1999 | 1999 |
| No of data (average) | 7 | 18 |
| No of data (max) | 12 | 40 |
| No of data (min) | 2 | 2 |
| Typical volume based value | Dust from milling | Dust from micronising |
| mg/Nm ³ (average) | 12 | 27 ^(*) |

^(*) When data from 2001 are taken into account, a typical volume based value for dust from micronising is 20 mg/Nm³, mainly due to improvement at one site.

Table 3.46: Dust emissions from the finishing section – TiO₂ production, the sulphate process [20, CEFIC-TDMA, 2004], [85, EIPPCB, 2004-2005]

Dust emissions during jet milling are subject to careful control. Since all plants use similar equipment, it is presumed that the variation in the data is due to operational reasons.

3.3.3.3.7 Abatement systems atmospheric emissions – the sulphate process

It should be noted, as shown in Figure 3.5, that the SO₂ from a filter salts roasting plant is considered to be treated according to the information given in the BREF on LVIC-AAF.

3.3.3.4 Emissions to water

3.3.3.4.1 Hydrolysis, filtration and washing

The major aqueous emissions are allocated to the filtration and washing section, specifically washing since the 'strong acid', which is the product of the filtration section (originating from the primary titanyl sulphate hydrolysis) and is forbidden by the TiO₂ Harmonisation Directive [21, The Council of the EU, 1992] to be discharged into the aqueous environment.

It should be noted that the concentration of sulphate and most of the metal ions in the final plant effluent is dependent both on the amount of copperas and copperas related products that are extracted (refer to Section 7.5) and the level of effluent treatment. There is no difference in the type of emission whether neutralisation or acid recycling has been used, however, it is possible to achieve a lower level of contaminants with neutralisation. As illustrated in Table 3.47, there are no other significant emissions to water from the process, except for suspended solids and sodium sulphates from the finishing section, which are given below. Sodium sulphate originates from caustic and caustic based agents, which are used to deposit the surface coating on the pigment. Sulphate and metals are the ions of concern and these are monitored closely in all countries.

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| No of data (min) | 2 | 2 |
| Typical volume based value | Dust from milling | Dust from micronising |
| mg/Nm ³ (average) | 12 | 27 ^(*) |
| (*) When data from 2001 are taken into account, a typical volume based value for dust from micronising is 20 mg/Nm ³ , mainly due to improvement at one site. | | |

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| Treatment method | Acid recycling or neutralisation | | | | | |
|-------------------------------------|----------------------------------|------|----------|----------|----------------|------------------|
| | Sulphate | Iron | Cd | Hg | Other metals * | Susp. solids |
| Collection period | 1999 | 1999 | 1999 | 1999 | 1999 | 1999 |
| kg per t TiO ₂ (average) | 274 | 18 | 0.000799 | 0.000310 | 3 | 12 |
| kg per t TiO ₂ (max) | 730 | 158 | 0.003200 | 0.002200 | 17 | 41 |
| kg per t TiO ₂ (min) | 30 | 0 | 0.000001 | 0.000000 | 0.001 | 0.09 |
| No of data (average) | 296 | 335 | 65 | 65 | 155 | 4579 |
| No of data (max) | 1095 | 1095 | 365 | 365 | 730 | 35040 |
| No of data (min) | 12 | 12 | 4 | 4 | 1 | 12 |
| Typical volume based values | Sulphate | Iron | Cd | Hg | Other metals | Suspended solids |
| mg/litre | 5151 | 259 | 0.022 | 0.0089 | 58 | 213 |

* Other metals are: Manganese (Mn) Vanadium (V) Titanium (Ti) Zinc (Zn) Chromium (Cr) Lead (Pb) Nickel (Ni) Copper (Cu) Arsenic (As)

Note: As stems from the figures provided by UBA-Germany, German plants performed better as, apart from Cadmium (Cd), all the other maximum load figures (sulphate, iron, mercury, and suspended solids) were lower, the maximum load of 'other metals' being 1 kg/t TiO₂, with a load of 0.05 kg Cr/t TiO₂ pigment.

Table 3.47: Major aqueous emissions from the TiO₂ production based on the sulphate process [20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [85, EIPPCB, 2004-2005]

The following are comments on particular emitted ions:

Sulphate: This is a key prescribed variable in the TiO₂ Harmonisation Directive [21, The Council of the EU, 1992] where the maximum allowable emission level is 800 kg/t TiO₂. The lower the level, the more effluent treatment that is carried out. There is a baseline sulphate concentration of ~100 kg/t which results from sodium sulphate from the coating process mentioned above.

It is known that the plants with the highest sulphate emission have projects in hand to reduce the current level by a further significant amount. Plants discharging into the Mediterranean Sea have, for many years, been special cases where the State regulatory authorities require total treatment. The same is now true for the Baltic Sea. This accounts for the lower end of the range. Similarly plants that discharge into the Rhine have special limits but in this case the controlling variable is the chromium content (see 'other metals' below).

Iron: This has been singled out of the metals since it is the major metal next to titanium in the original ilmenite ore (the formula of pure ilmenite is FeO·TiO₂).

Mercury and Cadmium: Data are given on these metals because they are the so-called 'black list' metals because they are the most ecotoxic. Fortunately the emissions are very low and are approaching the limits of detection of normal analytical methods. It is likely that the primary source of these metals is sulphuric acid rather than titaniferous ore.

It is believed that they are not affected by normal effluent treatment. To give these values a perspective, on average there is less than one gram emitted for every tonne of TiO₂ produced.

Other Metals (Mn, V, Ti, Zn, Cr, Pb, Ni, Cu, As): These are included to ensure that there is a perspective on all potentially harmful emissions. In general, the concentration of these ions (like iron and sulphate) is dependent on the source of the ore and the extent of the effluent treatment.

3.3.3.4.2 Finishing

Suspended solids (insoluble TiO₂) are the only significant emission to water, which are included in the last column of the Table 3.47 above.

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3.3.3.5 Solid wastes

3.3.3.5.1 Clarification and crystallisation

The unit quantity of neutralised digester residue is primarily a function of the unsulphateable impurity content of the feedstock. This is usually mainly a function of the silica content. Data on waste to land relating to neutralised digester residue are given in Table 3.48.

| Waste to land | |
|-------------------------------------|--------------------------|
| Treatment method | Neutralisation with lime |
| Emitted substance | Neutralised residue |
| kg per t TiO ₂ (average) | 307 |
| kg per t TiO ₂ (max) | 420 |
| kg per t TiO ₂ (min) | 180 |

Table 3.48: Waste to land from the digester residue (for TiO₂ production via the sulphate process) [20, CEFIC-TDMA, 2004]

3.3.3.5.2 Abatement systems for aqueous emissions from the sulphate process

Wastes to land mainly from the neutralisation of aqueous emissions from the sulphate process are given in Table 3.49.

| Wastes to land | | | | | |
|---------------------------------|---------------------|-------------------------------|--------------------------|----------------------|--------------------------|
| Treatment | | Neutralisation limestone/lime | Neutralisation limestone | Roaster | Neutralisation limestone |
| Emitted | Neutralised residue | Red gypsum | White gypsum | Roasted filter salts | Neutralised filter salts |
| kg/t TiO ₂ (average) | 117 | 3849 | 0 | 196 | 1327 |
| kg/t TiO ₂ (max) | | 6918 | 0 | | |
| kg/t TiO ₂ (min) | | 1113 | 0 | | |

Table 3.49: Wastes to land from the neutralisation of aqueous emissions, the sulphate process [20, CEFIC-TDMA, 2004]

This is a complex situation since, in the short to medium term, the amount of waste disposed to land is a function of a number of different factors:

- the effluent treatment process
- the success of the co-product marketing strategy, and in some cases
- commitments to landfill contracts.

Looking at the data for each substance:

Red gypsum: The range of tonnage here is dependent on a number of factors connected with the feedstock type and its mode of processing as indicated above in the section on acid usage. However, it is also dependent on the success that any site has on marketing it as a co-product. In some geographical areas, where there are old quarries that need to be filled with inert material, there may be a strong demand for red gypsum and the tonnage disposed to landfill could be substantially reduced or even eliminated.

White gypsum: It can be seen that the quantities disposed of to land are zero. This is because it is all used as a commercial co-product for the production of plasterboard.

Roasted filter salts: Data from one site.

Neutralised filter salts: Data from one site.

3.3.3.6 Environmental performance – Grimsby Works 2002

The purpose of this case study is to help bridge the gap after 1999 when the original performance data was collected.

The year 2002 was the first full one of operation on the new Combined Heat and Power (CHP) plant [86, The Council of the EU, 2004] and the new sulphuric acid import facility. This major restructuring of the energy supply to the site and the source of a critical raw material achieved all of its key objectives, primarily in making a massive reduction in emissions from the site, and also in simplifying the operation and improving business performance at the site.

Figure 3.6 gives the overall production balance for 2002 in Grimsby, illustrating major inputs and outputs from the titanium dioxide production process based on the sulphate process route.

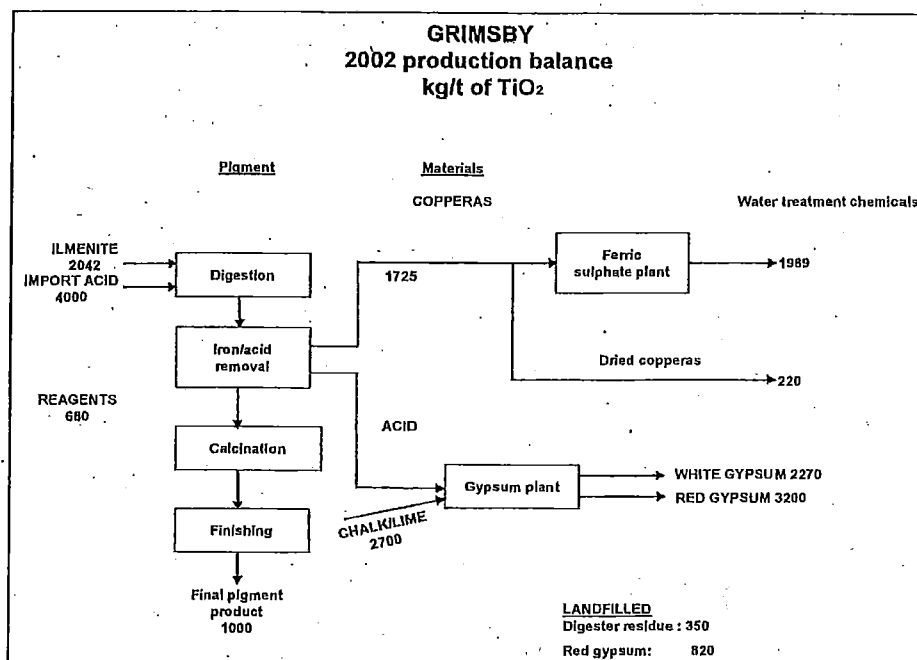


Figure 3.6: Main raw materials inputs and production outputs – the Grimsby site, 2002 [20, CEFIC-TDMA, 2004]

Emissions inventory

In the 2001 site report, major reductions in the emissions of SO_x, NO_x and particulates were predicted as a result of the combined heat and power and the sulphuric acid import projects. These allowed the closure and decommissioning of the on-site boiler plant and acid production plants – the major sources of these emissions. The first year of full operation of these two projects has fully demonstrated these reductions, as follows:

Sulphur oxides

The overall site emission of sulphur oxides, SO_x, decreased by 84 % during 2002. These improvements are only the latest in a series of Grimsby Works initiatives to reduce SO_x emissions since the early 1990s. Pigment calcination now accounts for over 99 % of all SO_x released from the site.

Nitrogen oxides

The overall site emission of nitrogen oxides (NO_x) decreased by 89 % during 2002. This was due to the closure of the boiler plant and the decommissioning of the original gas turbines at the gypsum plant. Again, pigment calcination is now the largest source of NO_x emissions – 77 % of the total.

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Hydrogen chloride (HCl)

The two site sources of HCl are the dilution of titanium tetrachloride and the preparation of TiO_2 nuclei (by reacting sodium hydroxide with dilute titanium tetrachloride). Both areas now have new scrubbing systems. The upgraded scrubber at titanium tetrachloride dilution was commissioned in 2002 and the total site HCl emissions have now been reduced from 2 tonnes in 2001 to 8 kilograms in 2002.

Carbon dioxide (CO₂)

The on-site emissions of carbon dioxide (CO₂), the main contributor to global warming, showed a decrease of 44 % in 2002. This CO₂ originates from fuel use and as a by-product from the neutralisation of acidic waste streams to form gypsum.

Carbon dioxide emissions associated with the TiO_2 production in the Grimsby Works in the period between 1997 – 2002 are illustrated in Figure 3.7.

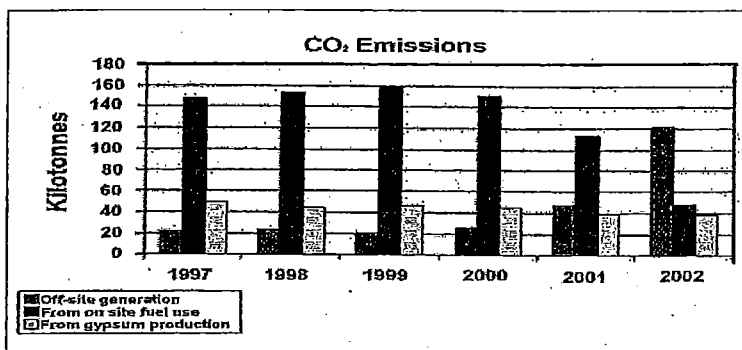


Figure 3.7: CO₂ emissions related to TiO_2 production in the Grimsby Works, the sulphate process [20, CEFIC-TDMA, 2004]

Carbon monoxide (CO)

Carbon monoxide (CO) emissions have fallen by 91 %. The only significant source on-site is now the white gypsum dryer.

Particulates (dust/droplets)

There was a reduction of 67 % from 2001 in the amount of particulates released. There are many emission points that contribute to this total such as ilmenite milling, pigment drying and pigment milling. The largest source had been incomplete combustion of heavy fuel oil in the site boiler plant. With the boiler plant decommissioned, the particulate emissions have dropped significantly. During 2002, several projects to reduce droplet emissions were completed.

Liquid effluent emissions

The reduction in these emissions was achieved by increased treatment (neutralisation) of plant effluent streams. The site has set a target for 2003 to consolidate the sulphate discharge at this figure and has set daily/weekly limits on the concentrations of a number of species in liquid effluent mainly acid, solids and metals.

Liquid effluent sulphate concentration in the Grimsby Works in the period of 1995 – 2002 is illustrated in Figure 3.8.

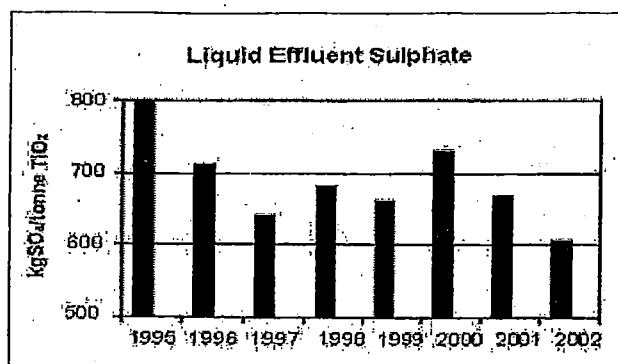


Figure 3.8: Liquid effluent sulphate load from TiO₂ production via the sulphate route in Grimsby Works
[20, CEFIC-TDMA, 2004]

Non-renewable resources

This area continues to be the focus of much attention. During 2002, the enormous benefits to the site in reduced unit energy consumption due to CHP plant operation have been realised. The site has also been able to set a new water consumption baseline for the new plant set up.

The site achieved a reduction of 18.7% (over the 2000 baseline) in unit energy consumption. This puts the site in a very strong position to meet its objective of a 25% reduction in unit energy consumption by the end of 2005. Unit energy consumption for 2000–2002 for the TiO₂ production at the Grimsby Works is illustrated in Figure 3.9.

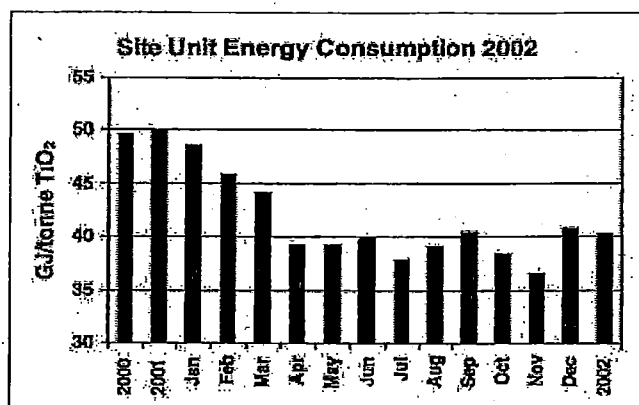


Figure 3.9: Unit energy consumption from TiO₂ production via the sulphate route in Grimsby Works
[20, CEFIC-TDMA, 2004]

Water usage

The total site water consumption was 6.13 million m³ per year. This is a very small (2%) overall increase from 2001. However, the unit water usage fell by 13% from 115.9 m³/tonne TiO₂ to 100.4 m³/tonne TiO₂.

Increased level of acid recycling

The acid recycling figure for 2002 was 8.0% which achieved the target. The target in 2003 was based on an acid/ilmenite ceiling in order to control sulphate input to site.

Detailed annual emissions 2002 in the Grimsby Works (in kg/tonne TiO₂ pigment) are given in Table 3.50.

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| | 1999 kg/t TiO ₂ | 2000 kg/t TiO ₂ | 2001 kg/t TiO ₂ | 2002 kg/t TiO ₂ |
|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Discharges to water | | | | |
| SO ₄ total | 630 | 689 | 619 | 591 |
| H ₂ SO ₄ | 152 | 169 | 149 | 170 |
| Fe | 159 | 174 | 143 | 136 |
| Solids | 41 | 36 | 30 | 59 |
| Ti | 6 | 6 | 5 | 6 |
| Mn | 7 | 8 | 7 | 7 |
| V | 0.23 | 0.30 | 0.26 | 0.20 |
| Zn | 0.17 | 0.25 | 0.17 | 0.18 |
| Cr | 0.08 | 0.11 | 0.11 | 0.08 |
| Pb ^(b) | 0.009 | 0.009 | 0.010 | 0.009 |
| Cu | 0.020 | 0.022 | 0.022 | 0.020 |
| Ni | 0.023 | 0.028 | 0.011 | 0.013 |
| As | 0.003 | 0.001 | 0.001 | 0.001 |
| Cd | 0.0003 | 0.0004 | 0.0002 | 0.0004 |
| Hg ^(c) | 0.00002 | 0.00001 | 0.00001 | 0.00003 |
| Emissions to air | | | | |
| SO _x total | 37.9 | 38.1 | 33.4 | 0.0 |
| SO _x TiO ₂ | 7.7 | | | 4.7 |
| Particulates | 1.9 | 2.5 | 2.2 | 0.7 |
| NO _x | 6.0 | 5.8 | 5.2 | 0.5 |
| HCl | 0.0 | 0.0 | 0.0 | 0.0 |
| CO | 0.8 | 0.8 | 0.6 | 0.0 |
| CO ₂ (from off-site generation) ^(d) | 306 | 401 | 872 | 1979 |
| CO ₂ (from fuel) ^(d) | 2328 | 2363 | 2083 | 778 |
| CO ₂ (from the gypsum plant) | 673 | 699 | 713 | 616 |
| Wastes to land | | | | |
| Gypsum | 1329 | 1512 | 1586 | 819 |
| Neutralised digester residue | 303 | 352 | 360 | 348 |
| Misc. industrial wastes | 52 | 155 | 70 | 55 |
| Misc. hazardous wastes ^(a) | 4 | 9 | 9 | 7 |
| Recycled waste | 15 | 41 | 21 | 28 |
| Energy usage | | | | |
| GJ | 41 | 43 | 42 | 40 |

1GJ=1 x 10⁹ Joules or approximately 278 kWh. Energy use was calculated by converting total site energy consumption in kWh (for electricity and fuel) to GJ by conversion factors (at 34 % conversion efficiency). Data for 1992 to 1997 are available in the 1998 Grimsby site report.

(a) Special waste including acid plant catalyst, solvents, oils and greases.

(b) The concentration of lead in the effluent has been reported as less than the analytical instrument level of detection. Since 1994, the mass emissions have been recalculated using a standard detection limit figure for each year. There has been no change in detectable lead concentrations.

(c) Mercury emissions calculated from external Environment Agency analyses that have lower limits of detection than Huntsman Trioxide methods.

(d) Calculated using new factors proposed by the Chemical Industries Association for current Climate Change Levy reporting.

Table 3.50: Detailed annual emissions 2002 in Grimsby Works, the sulphate process [20, CEFIC-TDMA, 2004]

3.3.4 Techniques to consider in the determination of BAT – the sulphate 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 the 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 3.51:

| 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 3.51: Information breakdown for each technique described in this section

Reference is to be made here also 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).

3.3.4.1 Raw material choice from import

Description

The general principle of choosing ores with as low as practical impurities is advisable. The choice of slag or ilmenite at one level is an LCA question (refer to Section 3.4.5), however, once this basic choice is made, and it is optimally made before starting the investment in a new plant, as it usually fixes the long term co-product marketing strategy. Typically there is limited chance to switch from ilmenite to slag or vice versa, because of capacity reasons, co-product management or availability of acid feed of different concentrations. However it is possible to use a blend of ilmenite and slag (refer to Section 3.3.3.1.1), or to digest ilmenite and slag separately combining the resulting liquor, but only within narrow limits.

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Achieved environmental benefits

The choice of titaniferous ores with a low content of impurities results in the minimisation of wastes released from TiO₂ production on the environment. At the TiO₂ production site, the use of slag gives rise to less waste from TiO₂ production. However, some TiO₂ producers are able to find uses for these 'waste' streams. In order to assess the impact on the environment as a whole, cross-media effects need to be taken into consideration.

Cross-media effects

From the point of view of environmental impact at the TiO₂ production site alone, the choice of titanium slag may appear to be a better long term strategy than the choice of ilmenite. However, the more pure the feedstocks for the production of TiO₂ (e.g. titanium slag), the more energy needed for the beneficiation of titaniferous raw materials and the more wastes generated at the supplier's site (refer to the life cycle assessment in Section 3.4.5).

Operational data

No detailed data submitted, in particular with regard to processing blends of slag and ilmenite, but since the cost of titanium slag is much higher than that of ilmenite, a thorough analysis of the material and energy efficiency of the process, including an overall assessment of the impact on the environment, and a detailed calculation of the manufacturing cost need to be carried out prior to any long term strategic decisions, e.g. revamping of the plant or a new TiO₂ plant built at the site.

Applicability

The choice of feedstock is applicable to all producers of TiO₂ pigments (in total in the EU-25, nine producers, 19 sites and 20 plants – see Table 3.5). It should be stressed that this technique is applicable, however, to some extent (as natural rutile is currently a very scarce raw material and the operators of the plants based on the chloride process use mostly synthetic rutile), to both the sulphate and chloride process routes.

Economics

No detailed data submitted apart from the LCA study included in Section 3.4.5.

Driving force for implementation

Decreased usage of energy and reduced impact on the environment at the TiO₂ producing site, counterbalanced by the higher prices of the upgraded titaniferous raw materials. This is a complex issue, and many factors should be considered, as indicated by the LCA.

Example plants

Fifteen European TiO₂ plants based on the sulphate process route, using either ilmenite or titanium slag or the blend of both (see Table 3.5).

Reference literature

[20, CEFIC-TDMA, 2004], [25, D.G. Heath, 1996], [26, EIPPCB, 2003], [70, Environment Agency, 1999], [21, The Council of the EU, 1992], [24, Tiioxide Group Ltd, 1995], [42, UBA-Germany, 2001], [48, W. Buchner et al, 1989], [85, EIPPCB, 2004-2005].

3.3.4.2 Raw material preparation

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. The ore is ground before further processing and, therefore, it cannot be wet, as the performance of the grinding section would then drop substantially, bottlenecking the TiO₂ production process. Also, the excessive content of moisture in the ore (ilmenite, titanium slag) may cause a warming-up and a premature reaction during the mixing of the ore with sulphuric acid in the digestion section (refer to Section 3.3.4.3). Therefore, if the ore becomes wet in transit, it must be dried before further processing, and this entails the use of energy with associated emissions of combustion products. Milling ilmenite to an optimum size maximises the efficiency of sulphation and, therefore, saves resources. In ore preparation, dust emissions are best controlled using high integrity bag filters with appropriate filter cloth material and a maintenance routine to minimise dust emissions.

Achieved environmental benefits

Less energy required for drying (and grinding) the titanium ore delivered with a low moisture content and, therefore, less CO₂, SO_x and NO_x emissions, that would otherwise result from the generation of an additional amount of energy required for drying more humid ore.

Cross-media effects

Increased amounts of dust may be expected when the titaniferous ore is handled in a dry state.

Operational data

The ore (ilmenite, titanium slag) is dried to a humidity content of <0.1 % [42, UBA-Germany, 2001]. Dust and NO_x emission levels are as presented in Section 3.3.3.3.1. Specific emissions of dust to air are in the range of 0.0002 to 0.08 kg/t TiO₂ [20, CEFIC-TDMA, 2004], the maximum emissions of dust to air being reported at the level of 4 kg/t TiO₂ [42, UBA-Germany, 2001]. Specific emissions of NO_x to air are in the range of 0.002 to 0.04 kg/t TiO₂ [20, CEFIC-TDMA, 2004].

Applicability

This technique is applicable to all TiO₂ plants using the sulphate process route.

Economics

No data submitted.

Driving force for implementation

Reduced emissions from drying. Better performance of the grinding section. Controlled reaction in the digestion section.

Example plants

Titanium dioxide plant in Grimsby, UK.

Titanium dioxide plants in Leverkusen (sulphate process route), Nordenham, Uerdingen, and Duisburg, which are all in Germany.

Reference literature

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

3.3.4.3 Digestion of the ore

Description

In the batch digestion process, the ground titaniferous material reacts with sulphuric acid, normally to 80 – 95 %. However, different streams of sulphuric acid are used, with concentrations from 70 %, through 80 %, to 96 %. The concentration of the added acid varies between 92 and 106 % [20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001].

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After achieving the required temperature, the cake has to ripen for 1 – 12 hours, depending on the raw material used, in order to reach the highest possible yield. During the digestion of titaniferous ore, off-gases are generated. These off-gases contain SO_2 and H_2S . The batch system is connected to a high efficiency scrubbing system, in which off-gases are treated before being released to the atmosphere. The cake obtained by digestion of the ore in sulphuric acid is then dissolved in cold water or diluted acid in temperatures below 85°C , in order to avoid a premature hydrolysis. The TiO_2 concentration in the obtained solution lies between 8 – 12 % (ilmenite digestion) and 13 – 18 % (titanium slag decomposition).

It should be noted that there is a large amount of expertise within the industry in optimising the batch process for maximum efficiency where several interdependent processing variables have to be set for every new ore import (e.g. ore fineness, acid concentration and batch time, linked with balances between concentrated, recycled and fresh sulphuric acid). Maximising the proportion of recycled sulphuric acid used is generally a good principle. If the recycled acid is too dilute, the chemical efficiency of digestion is lost. Digestion is a virtually unique process and the operators need to keep all the conditions for any particular ore or ore blend stable to ensure maximum chemical reaction efficiency. Also, it is necessary to obtain a cake texture that is capable of easy solubility. High efficiency digestion is almost a unique process because it involves heating a concentrated slurry (to initiate an exothermic reaction) that changes to a solid state, and then the last vital stages of conversion of the titanium atoms into a soluble matrix occur in the solid state. Experiential skill in the batch digestion of the ore has been developed over many years of operation. Failed digester batches pose a very high burden on the plant's disposal and effluent treatment systems.

Achieved environmental benefits

The batch process of decomposing ilmenite (or titanium slag) is of key importance for achieving a high yield of the titanium content in the ore to titanyl sulphate (TiOSO_4), and then to TiO_2 in the solution, which determines a high overall efficiency of the process, and contributes to reducing the impact of TiO_2 production on the environment. Also, diluted sulphuric acid can be reconcentrated in the process and recycled to the digestion section, thus reducing the usage of concentrated sulphuric acid (92 – 96 % H_2SO_4 , used for the digestion of ilmenite) or oleum (104 - 106 % H_2SO_4 , used for the digestion of titanium slag).

Cross-media effects

No information submitted.

Operational data

For information on off-gas treatment from digestion refer to Section 3.3.4.10.1. Data on waste to land relating to neutralised digester residue are given in Table 3.48 (the range of waste to land being reported between 180 – 420 kg/t TiO_2 , with the average figure of 307 kg/t TiO_2). Data on waste to land relating to neutralised digester residue in Grimsby Works in the period between 1999 and 2002 are given in Table 3.50. In turn, specific volumes of digester residues reported are in the range between 340 – 670 kg/t TiO_2 produced.

Although seemingly there appears to be no significant environmental differences between batch and continuous digestion (which is only applicable with ilmenite as a feedstock), continuous digestion has been tried, but it is unlikely that it can achieve the chemical efficiency of the batch process and, therefore, the batch digestion system is considered a key technique applied in the sulphate process (refer also to Section 9.3.2.1).

Applicability

Applicable to all TiO_2 plants using the sulphate process route.

Economics

No data submitted.

Driving force for implementation

High overall efficiency of the sulphate process.

Example plants

Titanium dioxide plant in Grimsby, UK.

Titanium dioxide plants in Leverkusen (sulphate process route), Nordenham, Uerdingen, and Duisburg, which are all in Germany.

Reference literature

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

3.3.4.4 Reduction

Description

When the primary ore is ilmenite (or a blend of slag with ilmenite) the digester liquor is contacted with scrap iron chips or a Ti^{3+} solution in order 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 technique, applied particularly to prevent the precipitation of the Fe^{3+} ions during the hydrolysis, involves setting the reduction level (as Ti^{3+}) so that a small excess of this component is maintained through the filtration and washing stages. A custom built system that allows efficient contact between the liquor and the iron and easy removal of any non-iron materials is typically used in the reduction section. Waste iron products can be used with obvious environmental advantages. As mentioned in Section 3.3.2.3, appropriate and clean scrap iron only can be used. The scrap must be free of contaminants.

Achieved environmental benefits

Usage of waste scrap iron, which is later crystallised out and recovered in the form of iron sulphate heptahydrate (copperas, used for waste water treatment or iron oxide, used as a pigment – see Section 7.5).

Cross-media effects

The process generates small amounts of gaseous hydrogen, which should be dealt with properly to prevent the risk of explosion.

Operational data

Reported emissions of hydrogen are in the range between 0 – 2 kg per tonne of TiO_2 produced. Usage of scrap iron is in the range between 127 to 250 kg/t TiO_2 .

Even though the quantities involved limit the risk well within the boundary of the plant area (hydrogen is instantly dispersed in air and, therefore, the explosion risk is extremely low), the equipment should be designed to work in a flammable atmosphere and proper venting of the building is required.

Applicability

Applicable to all plants based on the sulphate process route which use ilmenite, as well as to plants using a blend of slag with ilmenite, which also use scrap iron dosage.

It is noted that one plant blends liquor from slag digestion with the unreduced liquor of ilmenite digestion and thus uses no scrap iron.

Economics

No data submitted.

Driving force for implementation

Performance of the sulphate process, when ilmenite is a raw material.

Example plants

Titanium dioxide plant in Grimsby, UK.

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Reference literature

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

3.3.4.5 Clarification and crystallisation

Description

After the reduction of ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}) in the solution of titanyl sulphate, two operations need to be performed: the removal of suspended materials from the solution by flocculation and filtration (clarification of the titanyl sulphate solution), followed by the crystallisation and removal of iron sulphate heptahydrate.

The disposal route for the solids must be looked at carefully since the options available are usually dictated by the impurity content and type. In the clarification section, all insoluble solids are separated from the solution by flocculation and filtration. The solid residue is neutralised with lime or limestone and, in most cases, is sent to landfill, as there is only a very limited market for this residue as a co-product. Normal practice is to have a system that allows efficient separation of the flocculated solids and it is necessary to optimise the system for particular ore feedstocks. It should be noted that stable liquor is a prerequisite for an efficient operation. The use of pressure filters for the dewatering of digester residue is considered.

After the removal of all insoluble solids, the solution contains 5 – 6 % FeSO_4 in the case of processing titanium slag and 15 – 20 % FeSO_4 in the case of processing ilmenite and ilmenite enriched with slag, and in the latter case, iron sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), i.e. copperas, is crystallised by vacuum cooling in the crystallisation section.

The separation of copperas is the most environmentally efficient way of removing iron, especially as there is an internationally established market for copperas, particularly for the manufacture of water treatment chemicals (refer to Section 7.5). For ilmenite liquors, various crystallisation arrangements are possible. Normally the objective is to maximise the removal of copperas. There are no significant environmental differences reported between batch and continuous centrifuges (crystallisers), however, the latter can be very difficult to commission and optimise to give maximum separation efficiency.

Achieved environmental benefits

The major environmental benefit in this section is the removal of iron from the process in the form of copperas (iron sulphate heptahydrate), which can be subsequently used for waste water treatment or, after salt roasting, converted into iron oxide (Fe_2O_3), which then finds applications as an iron oxide pigment. Copperas production is an environmentally benign process since every tonne that is produced and used relieves the need for subsequent treatment of the main TiO_2 plant effluent.

Cross-media effects

As there is a very limited market for the insoluble solids originating from the clarification section, the neutralised solids are typically landfilled. Waste to land varies in the range between 180 - 420 kg per tonne of TiO_2 produced. In the case of copperas roasting to Fe_2O_3 in a downstream unit, the emission of gaseous SO_2 has an additional negative effect, however, the SO_2 gas can be used for the production of sulphuric acid at the same site.

Operational data

No detailed data submitted. Refer to Section 7.5 on 'Copperas and related products'. The major EU-15 producers of ferrous sulphate heptahydrate are listed in Table 7.17. The combined EU-15 production capacity of the ferrous sulphate heptahydrate amounts to over 1.1 million tonnes per year.

Applicability

Applicable particularly to the plants based on the sulphate process route which use ilmenite.

Economics

No data submitted.

Driving force for implementation

The separation of copperas (by crystallisation), allows for increasing the concentration of TiO_2 in the solution, and hence for a higher efficiency of TiO_2 production by the sulphate process route. The higher the process efficiency, the lesser the impact on the environment. In turn, the use of copperas, not only directly reduces the impact of TiO_2 production on the environment, but also allows for the manufacture of valuable by-products (value added).

Example plants

Titanium dioxide plant in Grimsby, UK.

Titanium dioxide plant in Prerov, Czech Republic.

Reference literature

[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [59, CEFIC-TDMA, 2004], [48, W. Buchner et al, 1989], [85, EIPPCB, 2004-2005].

3.3.4.6 Hydrolysis (hydrate precipitation)Description

After the crystallisation and removal of iron sulphate heptahydrate, the titanyl sulphate is hydrolysed by heating the clarified solution with steam at 95 to 110 °C. In order to achieve TiO_2 yields of up to 93 – 96 % and to obtain a hydrolysis product which yields the optimum particle size upon subsequent firing, special nuclei accelerating the precipitation of titanium hydrate are added at the beginning of the hydrolysis.

There are two nucleation systems used. In one, nuclei are created by controlled hydrolysis of titanium tetrachloride. In the other, the seed is produced by reacting TiO_2 slurry with NaOH and HCl. Changing from one system to another is problematic, because each system has unique characteristics with regard to the control of crystal size distribution. Controlled hydrolysis is one of the key variables in determining final product quality, hence there is considerable risk in incorporating changes which are designed, for example, to reduce energy consumption. Low concentration hydrolysis is one of these options, and the concentration used is usually dependent on the specific final quality requirements and the consistency of the ore feedstock.

Achieved environmental benefits

Apart from the possibility of achieving high TiO_2 yields of up to 93 – 96 %, which have a direct influence on the overall performance of the plant, no direct impact of this operation on the environment has been reported.

Cross-media effects

No information submitted.

Operational data

No data submitted.

Applicability

Applicable to all TiO_2 plants using the sulphate process route.

Economics

No detailed data submitted.

Driving force for implementation

High TiO_2 yields in the process and controlled size and form of the titanium dioxide crystals (anatase or rutile). Only the sulphate process can readily form both crystalline forms of TiO_2 (anatase and rutile crystals).

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Example plants

Titanium dioxide plant in Grimsby, UK.

Titanium dioxide plants in Leverkusen (sulphate process route), Nordenham, Uerdingen, and Duisburg, which are all in Germany.

Reference literature

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

3.3.4.7 Filtration and washing

Description

After the hydrolysis, the solution contains 20 – 28 % H_2SO_4 and different quantities of dissolved sulphates, depending on the raw material used. The titanium oxide hydrate is separated from the spent sulphuric acid by filtration. There are three possibilities for the utilisation of the spent post-hydrolytic sulphuric acid (refer also to Section 3.3.4.11):

- concentration of the spent acid to approx. 70 – 80 % H_2SO_4 and its re-use for the digestion of the titanium ore
- neutralisation of the spent acid with lime, which generates gypsum
- utilisation of the reconcentrated spent acid for the production of fertilisers.

After the separation of the spent acid, the titanium oxide hydrate is washed with water or a weak acid. After washing, the titanium oxide hydrate still contains 5 – 10 % H_2SO_4 . In order to obtain required pigment qualities, alkali-metal compounds and other mineralisators are added to the hydrate, which is then normally filtered consecutively in a vacuum filter and press filter, after which the cake with a content between 45 – 50 % TiO_2 is led into the revolving hearth furnace in the calcination section.

The filtered diluted sulphuric acids are collected in a storage, from where they can be recycled into the process or discharged as waste waters (refer to Section 3.3.4.11). The maximum amount of undiluted strong acid must be separated from the filter cake during washing. This section offers many opportunities to efficiently use different grades of water during the wash cycle. The system requires the sharpest separation of strong and weak acid. Fortunately tried and tested conventional leaf filters allow almost 'plug flow' of the strong acid during the first stage of washing hence achieving this objective. Many other filtration systems have been tried and found wanting. Often it is the sheer size and throughput requirements, which govern the choice of filtration system.

Achieved environmental benefits

Proper design and operation of the filtration and washing section has a direct influence on the separation of strong and weak sulphuric acid and, therefore, on the degree of acid recirculation in the process and the amount of waste waters generated in and discharged from the plant to the aquatic environment.

The impact on the environment varies, depending on the option applied for the utilisation of the spent post-hydrolytic sulphuric acid, however, for all options, the spent acid is utilised to a high degree (production of TiO_2 , production of gypsum plasterboards, and production of fertilisers), thus allowing to significantly reduce the amount of the sulphuric acid discharged to the environment.

Cross-media effects

No data submitted.

Operational data

For information on the utilisation of the spent sulphuric acid, refer to Section 3.3.4.11.

Applicability

Applicable to all TiO₂ plants using the sulphate process route.

Economics

No detailed data submitted (refer to Section 3.3.4.11).

Driving force for implementation

High degree of separation (and then utilisation) of the spent post-hydrolytic sulphuric acid.

Example plants

Fifteen European TiO₂ plants based on the sulphate process route, using either ilmenite or titanium slag or the blend of both (see Table 3.5).

Reference literature

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

3.3.4.8 CalcinationDescription

After filtration and washing, the hydrate is calcined in a revolving hearth furnace (calciner). Approximately 2/3 of the entire retention time of 7 – 20 hours is required for the drying process in the calcination section. At a temperature of approx. 500 °C in the revolving hearth furnace, SO₃ gas (originating from the H₂SO₄ remaining in the cake) is separated, which is partially decomposed into SO₂ and O₂. The product reaches maximum temperatures of 800 – 1100 °C. Due to the combustion of oil or natural gas in the furnace, the main combustion related gaseous emissions from the calcination section are SO₂ and NO₂, as well as dust. The temperature of the exhaust gas must be kept above 300 °C, in order to avoid the condensation of the H₂SO₄ in the gas outlet system, prior to its transfer for treatment either in the off-gas scrubber or catalytic oxidation system, or recycling into the furnace for saving energy. Maximum hot gas recycling is used when technically possible at the site. Systems that minimise energy usage without compromising quality are recommended. These include pressure filters on the feed (in order to increase the TiO₂ content in the cake) and hot gas recycling in the kilns (in order to save energy). For information on the off-gas treatment unit, refer to Section 3.3.4.10.2.

It should be noted that calcination is a unit operation characteristic only to the sulphate process route, and the calcination section does not exist in the chloride process (here, similar functions are performed in the oxidation section).

Achieved environmental benefits

Hot gas recycling used at the site to save energy is the only environmental benefit attributable to the calcination section. This section is, however, fully integrated with the off-gas treatment unit.

Cross-media effects

No data submitted.

Operational data

Refer to Sections 3.3.3.3.5 and 3.3.3.6.

Applicability

Applicable to all TiO₂ plants using the sulphate process route.

Economics

No data submitted on economics in the calcination section. For data on economics of the off-gas treatment, refer to Section 3.3.4.10.2.

Driving force for implementation

The quality of the titanium dioxide pigments (anatase or rutile).

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Example plants

Fifteen European TiO₂ plants based on the sulphate process route, using either ilmenite or titanium slag or the blend of both (see Table 3.5).

Reference literature

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

3.3.4.9 Finishing

Description

Finishing operations are, in principle, the same in both the sulphate and chloride process routes. The TiO₂ clinker obtained in the calcination section is cooled by air and is then ground. Off-gas containing fine particle TiO₂ dust is filtered in cloth filters, and then discharged into the atmosphere. As follow-up treatment (finishing) additives and water are added, this results in some emissions of sulphates and suspended solids to water.

In the finishing section, the operational technique is to maintain the plant to minimise leakage of TiO₂ to both air and water. It is well known that because of the intrinsic properties of the TiO₂ pigment, this area can be easily covered in brilliant white material. It is expected that in this context the plant is managed to prevent this happening. Spillage control and minimisation of dust emissions are essential. As this is a key area in both energy and water usage, the appropriate discipline and usage objectives must be sustained. Steam milling is essential to ensure the maximum efficiency of pigment usage in downstream applications. Minimising dust and emissions of TiO₂ particles in the liquid effluent is a necessary objective, but since all the equipment is similar regarding these, it is the management and maintenance regimes that are critical here.

Coating is required to maximise the efficiency and lifetime of downstream TiO₂ pigment uses. The use of pressure filters before drying under some circumstances can be considered, however, modern plants have usually opted for spray dryers as these give an excellent textured feed for micronising. Pressure filters can be followed by fluid bed dryers. It is worth noting, that bulk or semi-bulk packaging is best for minimising the use of packaging materials. It is, in principle, recommended, however only customers from large companies have the facilities to handle these containers.

Achieved environmental benefits

All major finishing operations, in which dry material is handled, are subject to dedusting, with the TiO₂ dust recycled back into the process.

Cross-media effects

No data submitted.

Operational data

Specific emissions of dust to air are in the range of 0.002 to 0.390 kg/t TiO₂. Dust emissions in Germany are reported to be at the levels of 0.002 to 0.12 kg/t TiO₂. Waste waters containing suspended solids in the range of 0.09 to 41 kg/t TiO₂ are reported. Germany reports the levels of sulphates in the waste waters in the range of 80 to 110 kg/t TiO₂.

Applicability

Applicable to all TiO₂ plants using either the sulphate or chloride process routes.

Economics

No data submitted.

Driving force for implementation

The quality of various grades of TiO₂ pigments, as required by the final users.

Example plants

Twenty European TiO₂ plants, including five plants using the chloride process route and fifteen European TiO₂ plants based on the sulphate process route (see Table 3.5).

Reference literature

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

3.3.4.10 Abatement systems for gaseous emissions – the sulphate process

This section covers abatement systems for gaseous emissions encountered in two main sections of the sulphate process route, namely the digestion section (see Section 3.3.4.10.1 below) and the calcination section (see Section 3.3.4.10.2 below). Dust emissions from the raw material preparation section and from the finishing section are covered in Sections 3.3.4.2 and 3.3.4.9 respectively.

3.3.4.10.1 Off-gas treatment from the digestion sectionDescription

Because of the specific nature of these systems, management must be focused on sustaining maximum efficiency. This can be problematic since the scrubbing system must cope with a very wide range of flows. The industry has installed custom built scrubbers designed to operate at the necessary very wide turn down. The modern systems are designed with energy and water saving in mind. There appears to be no significant differences between the following systems (depending on the local situation), as in some sites the off-gas treatment system from the ore digestion section is interconnected with that from the calcination section – see Section 3.3.4.10.2.

First, off-gases are scrubbed with recycled waste water (this system is only applicable if the feedstock is solely ilmenite). The outcoming wash-water has to be treated in an appropriate way.

Secondly, off-gases are quenched and then scrubbed with caustic soda solution. The resulting solution contains Na₂SO₄, NaHSO₃, Na₂S, and is decomposed with sulphuric acid to produce SO₂ and S going as a feed to the acid plant; the resulting small amounts of Na₂SO₄ solution is discharged. This system is only applicable if there is the possibility to use the SO₂ and S as a feedstock for other processes on the site.

Thirdly, off-gases are quenched and then scrubbed with caustic soda solution. Scrubbed caustic soda solution, after oxidation of NaHSO₃, is released to the sewerage system, and then it is sent to the waste water treatment plant located at the site.

Finally, off-gases are quenched, then passed through an electrostatic precipitator (removing SO₃ aerosols), followed by the removal of SO₂ via oxidation with aqueous H₂O₂ to produce sulphuric acid which is re-used, and finally removing H₂S by absorption in an aqueous suspension of ZnO, which is used as a feedstock for the production of Zn containing pigments at the same site. This is a patented waste free system but is only viable if there is a zinc based chemical business adjacent to the TiO₂ plant.

Achieved environmental benefits

Reduction of SO₂ and H₂S emissions from the sulphate process.

Chapter 3Cross-media effects

No data submitted. Possible integration with the adjacent sulphuric acid plant.

Operational data

Specific emissions of SO₂ to air are in the range of 0.00 (ilmenite) to 1.91 kg/t TiO₂ (titanium slag) [20, CEFIC-TDMA, 2004], the maximum emission of SO₂ in Germany being reported at the level of 0.119 kg/t TiO₂ [42, UBA-Germany, 2001]. Specific emissions of H₂S to air are in the range of 0.000 to 0.010 kg/t TiO₂ [20, CEFIC-TDMA, 2004].

Gaseous emissions treatment performance and costs for digestion are given in Table 3.52 below.

| Digestion | Slag | Ilmenite | Digestion | Slag | Ilmenite |
|---------------------|------|----------|-----------|-----------------------------------|-------------|
| kg/t | | | Site | Calais Scarlino Le Havre | Grimsby |
| SO ₂ | 1 | 0.2 | | | Huelva |
| H ₂ S | 0.01 | 0 | | | Pori |
| Costs: EUR/t | | | | | Leverkusen |
| Capital +/- 30 % | 85 | 75 | | | Nordenham |
| Treatment | 10 | 5 | | | Fredrikstad |
| | | | | Thann | |
| | | | | Prerov | |

Note: No data available for the sites using blends of slag and ilmenite.

Table 3.52: Gaseous emissions treatment performance/costs – digestion, the sulphate process [20, CEFIC-TDMA, 2004]

Applicability

Applicable to all TiO₂ plants using the sulphate process route.

Economics

As in Table 3.52 above.

Driving force for implementation

Minimisation of the impact of the production of TiO₂ on the environment.

Example plants

Titanium dioxide plant in Grimsby, UK.

Reference literature

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

3.3.4.10.2 Gaseous effluent treatment from the calcination sectionDescription

The following techniques used for gas treatment are generally considered now to be standard throughout the industry:

- dust is removed by scrubbing and then it is recycled
- SO₃ is removed by electrostatic precipitators
- the SO₂ component of the gas is catalytically oxidised to SO₃ and absorbed to form sulphuric acid, which in turn is recycled.

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There is an issue of economic impact here. The standard equipment for the catalytic oxidation of SO₂ is module based and provided there is the physical space, the number of units fitted is, on one hand, a question of economics and available resources, and on the other, it needs to be sufficient to achieve the statutory SO₂ concentration. In this context, the operational procedure involves keeping the catalyst as uncontaminated as possible by protecting it from dust ingress. Also, a monitoring and maintenance schedule is adopted in which the catalyst is renewed as required. Those sites that have alternative systems for treating the off-gas are organised such to treat it at all times.

There are other options but they are particular to local circumstances. For example, direct absorption of SO₂ in a sulphuric plant can be adopted, but this is only possible if there is a very short distance between the TiO₂ and sulphuric acid plants. A water-based system for the removal of SO₂ is used by one company, which is reported to have similar performance characteristics to the catalytic system. A system for the treatment of off-gas from the calciners is applied in Germany, in which fixed bed active carbon reactors-adsorbers are used, with the aim of keeping the emissions below the German limit value of <0.5 g SO₂/m³ [42, UBA-Germany, 2001].

Achieved environmental benefits

Reduced emissions of acid mist, dust, SO₂ and NO₂ from the sulphate process.

Cross-media effects

No data submitted.

Operational data

Gaseous emissions treatment performance and costs for calcination are given in Table 3.53.

| Calcination | Catalyst standard | Catalyst high | Scrubbing | Calcination | Catalyst standard | Catalyst high | Scrubbing |
|--|-------------------|---------------|-----------|-------------|---|---------------|--|
| Catalyst load* | | | | Site | Calais Scarlino Grimsby Huelva Prerov Pori | Duisburg | Leverkusen Nordenham Fredrikstad |
| m ³ /t per hour of TiO ₂ feed | 30 – 50 | 70 – 90 | | | | | |
| kg/t | | | | | | | |
| SO ₂ | 8 | 2 | 1 | | | | |
| Acid mist | 0.8 | 0.2 | 0.2 | | | | |
| Dust | 0.4 | 0.004 | 0.001 | | | | |
| Costs(EUR/t)** | | | | | | | |
| Capital +/- 30 % | 70 | 140 | 170 | | | | |
| Treatment | 5 | 10 | 9 | | | | |
| *Definition of catalyst load Volume of catalyst (V) TiO ₂ feed: t/h (T) m ³ /t per hour of TiO ₂ feed (V/T) **Definition of costs Capital for a new unit (C) Annual production (P) Capital (C/P) | | | | | | | |

Table 3.53: Gaseous emissions treatment performance/costs – calcination, the sulphate process [20, CEFIC-TDMA, 2004]

Acid mist, dust, SO₂ and NO₂ emission levels from calcination are as presented in Section 3.3.3.3.5. Specific emissions of dust to air are in the range of 0.00 to 0.65 kg/t TiO₂ [20, CEFIC-TDMA, 2004]. Specific emissions of SO₂ to air are in the range of 0.01 to as much as 12.10 kg/t TiO₂ (due to high emission levels in one plant in 1999), the average being 3.5 kg/t TiO₂ [20, CEFIC-TDMA, 2004], while the emissions of SO₂ in Germany being reported at the level of 1 kg/t TiO₂ [42, UBA-Germany, 2001]. In turn, the 2002 emissions of SO₂ reported by Grimsby Works are at the level of 4.7 kg/t TiO₂ (see Table 3.50). Specific emissions of NO₂ to air are in the range of 0.04 to 1.20 kg/t TiO₂ [20, CEFIC-TDMA, 2004].

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Applicability

Applicable to all TiO₂ plants using the sulphate process route.

Economics

Refer to Table 3.53 above.

Driving force for implementation

Minimisation of the impact of the production of TiO₂ on the environment.

Example plants

Titanium dioxide plant in Grimsby, UK.

Reference literature

[20, CEFIC-TDMA, 2004], [46, CEFIC-TDMA, 2001], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [85, EIPPCB, 2004-2005].

3.3.4.11 Abatement systems for aqueous emissions from the sulphate process

The sulphate process requires 2.4 – 3.5 tonnes of concentrated H₂SO₄ per one tonne of TiO₂ produced, depending on the raw material used. Sulphuric acid is discharged from the process in the form of sulphates, especially as ferrous sulphate (refer to Sections 3.3.4.5 and 7.5), or as a free sulphuric acid in the form of the spent post-hydrolytic acid. The total volume of the spent acid amounts to approximately 6 – 9 tonnes per one tonne of TiO₂ produced. Therefore, the treatment of the spent acid is one of the most important issues with regard to the impact of the production of TiO₂ by the sulphate process route on the environment [21, The Council of the EU, 1992].

It should be noted, that the load of sulphate (SO₄) to water is a key prescribed variable in the TiO₂ Harmonisation Directive [21, The Council of the EU, 1992], where the maximum allowable emission level is 800 kg of total sulphate per tonne of TiO₂ produced (corresponding to the SO₄ ions contained in the free sulphuric acid and in the metallic sulphates).

As mentioned in Section 3.3.4.7, there are three possibilities of the utilisation of the spent post-hydrolytic sulphuric acid:

- concentration of the spent acid to approx. 70 – 80 % H₂SO₄ and its re-use for the digestion of the titanium ore
- neutralisation of the spent acid with lime, which generates gypsum
- utilisation of the reconcentrated spent acid for the production of fertilisers.

Although in options 1 and 3 above, there are different final uses of the recovered sulphuric acid (production of TiO₂ vs. production of fertilisers), in both these options the abatement system for aqueous emissions is based on the concentration of the spent post-hydrolytic sulphuric acid and, therefore, only the following two main options are discussed below:

- acid recycling
- acid neutralisation.

These options are also illustrated in Figure 3.4, Figure 3.5, and Figure 3.6 respectively.

The separation of the sulphates from the spent post-hydrolytic acid, and follow-up thermal decomposition of the sulphates to Fe₂O₃, and to SO₂ which is used for the production of H₂SO₄, is described in Sections 3.3.4.5 and 7.5.

The operational technique for acid recycling involves, in principle, operating the plant in such a manner that at least all the strong acid produced is treated to achieve the statutory requirements. The quality and rate of the acid produced need to be suitable for maintaining TiO_2 plant production. If filter salts are roasted, then similar constraints apply both in feed rates and SO_2 production that needs to be fed to the sulphuric acid plant. Also, the quality of the cinder produced needs to be satisfactory for its downstream use whether this is for co-products or disposal. In the same way, neutralisation needs to be set up to achieve similar objectives, as both plant throughput and co-product quality are key variables.

The issue of co-product quality often has a profound effect on the operability of the plant since obtaining and sustaining this quality needs the plant design and operation to be optimised to guarantee this quality. With gypsum, particularly where the co-product is used in plasterboard manufacture, it was necessary to carry out a large amount of development work to optimise the properties of gypsum (mainly crystal shape) to enable efficient production of plasterboard. This itself often reflects back on the operation of the mother titanium dioxide plant. It is essential to avoid the situation where these constraints on the two plants are in conflict.

Although landfill is considered to be undesirable as a generalisation it should be said that titanogypsum is an almost ideal landfill material and sometimes local circumstances need quarries, etc. to be reclaimed with an 'inert' material, such as titanogypsum which does not have the disadvantages of most other types of waste products [20, CEFIC-TDMA, 2004].

Both acid recycling and neutralisation, are the methods to be considered for use in the titanium dioxide industry for liquid effluent treatment, provided they are set up to take into account the factors listed in Table 3.54, as the decision of which method to choose is dependent on them:

| Treatment method | Acid recycling | Neutralisation |
|---|---------------------------|--|
| Capital cost | High | Lower |
| Running costs | +15 % | +15 % |
| Extra energy consumption | +13.8 GJ/tonne TiO_2 | +2.3 GJ/tonne TiO_2 |
| Opportunity for an effective local co-products strategy to be developed | Helpful but not essential | Essential |
| Ore supply | | Stable and consistent to maintain co-product quality |
| Waste disposal | Local facilities helpful | Local facilities essential |
| Neutralising materials | | Local supply required to keep costs down |

Table 3.54: Methods used for liquid effluent treatment, the sulphate process
[20, CEFIC-TDMA, 2004]

Table 3.54 indicates that the choice of treatment is a long term strategic one in which local conditions (commercial, legal, industrial infrastructure, raw materials availability, etc.) will be strongly influential.

It should be added that in various EU countries (e.g. UK and Italy), the usage of red gypsum in agriculture has been accepted by the authorities. In other countries (e.g. Germany), this is not possible. Therefore, different techniques develop, also because of different national legislation applied across the EU-25 [85, EIPPCB, 2004-2005]. Refer also to Section 3.3.4.11.2 below.

The choice between waste acid recycling and waste acid neutralisation, and the decision upon which of the methods is to be applied, will depend on local conditions, including the availability of secondary feedstock (chalk, lime) and market conditions for co-products.

The data on the methods used for acid treatment, illustrating strong and weak effluent treatment costs and performance, are given in Table 3.55.

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| | Strong + weak acid | | | |
|--|--|---------------------------------|----------------------------|--|
| | Acid recycling + roasting | Acid recycling + neutralisation | Neutralisation at pH 7**** | Neutralisation at pH9 |
| Water emissions kg/tonne | | | | |
| Total sulphate as SO ₄ | 500 ^o | 400 | 400 | 300 |
| Fe | 8 ^o | 3 | 3 | 0.1 |
| Waste to land kg/tonne | | | | |
| Cinders | 0 – 500* | | | |
| Neutralised filter salts | | 0 – 1300 | | |
| Red gypsum | | 0 – 1200* | 2000 – 6000** | 3000 – 7000** |
| Cost: EUR/t | | | | |
| Capital replacement | | | | |
| Cost +/- 30 % | 1800 | 1200 | 700 | 800 |
| Treatment | 150 | 150*** | 150*** | 170*** |
| Site | Calais Duisburg Nordenham Leverkusen Uerdingen | Huelva Pori | Grimsby Le Havre | Scarlino Prerov Fredrikstad Thann |
| * The quantity varies with the local ability to re-use as co-product | | | | |
| ** The quantity of red gypsum produced varies with the white gypsum production, which is sold as a co-product, and on the ability to use red gypsum for land reclaiming | | | | |
| *** These costs are largely affected by the amount of red gypsum to be landfilled and transport costs from production to land disposal area | | | | |
| **** Final reactor pH | | | | |
| ^o In order to achieve lower values of iron and sulphate than is shown here, quite a large amount of energy would have to be involved in evaporating the weak acid, and a neutralisation unit may be needed. | | | | |

Table 3.55: Strong and weak acid effluent treatment costs and performance [20, CERIC-TDMA, 2004]

The two main techniques used in the European titanium dioxide industry, which are presented below in Section 3.3.4.11.1 (waste acid recycling) and in Section 3.3.4.11.2 (waste acid neutralisation), apply to all fifteen EU-25 TiO₂ plants based on the sulphate process route. However, no information is available, which shows the method of the spent acid treatment applied in the titanium dioxide plant in Celje, Slovenia.

3.3.4.11.1 Waste acid recycling

Description

Refer to the general description in Section 3.3.4.11 above.

A method available for strong waste acid is to optimise the re-use of the concentrated waste acid in the digestion step and/or to sell surplus amounts as a co-product. A method available for weak acid is to optimise its re-use in the process or to neutralise it.

In this area it is appropriate to make the following point on the risks involved in transferring techniques between different sites: TiO₂ pigments are highly quality focused and every plant was built and developed to meet the quality requirements and to compete with the quality of pigments produced at other sites with different technologies. Every improvement in most environmental aspects has an influence on pigment quality (e.g. using concentrated recycled waste acid means a higher input of trace elements into the digestion step, and this has to be equalised by the improvement of washing steps) and needs quite a large capital investment.

So nearly every improvement on the environmental side should be tailor made for only one site in close contact with the supplier of a new technique, as the transfer to another site without further fitting does not guarantee any success.

Achieved environmental benefits

The total volume of the spent acid amounts to approximately 6 – 9 tonnes per one tonne of TiO₂ produced. Therefore acid regeneration, concentration and recycling has a direct positive impact on the environment. When the acid is recycled back to the digestion section, also the usage of fresh input sulphuric acid for the production of TiO₂ pigments is reduced. At the same time, the operation of acid neutralisation with lime is avoided, which – in certain unfavourable conditions – may lead to the generation of large amounts of waste red gypsum.

Cross-media effects

A large amount of energy is required (see Table 3.54 above) for the concentration of the spent sulphuric acid (from approx. 20 % to approx. 70 – 80 %). The more additional energy used, the larger the emissions of CO₂, SO₂, NO_x and dust resulting from its generation.

Operational data

Data concerning aqueous emissions, covering both acid recycling or neutralisation, are given in Table 3.47. Refer also to Sections 3.3.4.5 and 3.3.4.7, and see Table 3.54 and Table 3.55 above.

However, the most characteristic for this technique are the data from German TiO₂ producers, as all of them are using the method of waste acid recycling. According to data from Germany, the following are specific loads, on the annual average level, for the process waste water from the filtration and washing section:

| | | | |
|--------------------|-----------------|---------|------------------------|
| • SO ₄ | 30 – 300 kg/t | average | 122 kg/t |
| • Fe | 0.25 – 5 kg/t | average | 2 kg/t |
| • Cd | 0.001 – 3 g/t | average | 0.001023 g/t |
| • Hg | 0.00032 – 1 g/t | average | 0.000339 g/t |
| • other metals | 0 – 1 kg/t | average | 1 kg/t (maximum value) |
| • suspended solids | 1 – 5 kg/t | average | 3 kg/t. |

In particular, based on actual data from the German plants, the specific loads of some heavy metals in the group of 'other metals' can be split as follows: Cr: <50 g/t; Pb: <30 g/t; Cu: <20 g/t; and Ni: <15 g/t of TiO₂ pigment produced.

The official monitoring of one German plant shows the following 2004 (annual average) data on the specific loads of heavy metals: Cr 36 g/t, Pb 3 g/t, Cu <8 g/t, Ni <2 g/t, Cd <0.7 g/t, Hg <0.07 g/t TiO₂ pigment produced.

At the same time the sulphate load in the process waste water from the finishing section amounts to:

| | | | |
|-------------------|---------------|---------|----------|
| • SO ₄ | 80 – 110 kg/t | average | 95 kg/t. |
|-------------------|---------------|---------|----------|

Applicability

In principle, applicable to all TiO₂ plants using the sulphate process route (refer to the explanations included in Section 3.3.4.11).

Waste acid recycling is, in principle, an option mutually excluding with the option of waste acid neutralisation (see Section 3.3.4.11.2).

Economics

As in Table 3.54 and Table 3.55 above.

Driving force for implementation

The protection of the environment.

Example plants

Titanium dioxide plants in Leverkusen (sulphate process route), Nordenham, Uerdingen, and Duisburg, which are all in Germany.

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Reference literature

[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [48, W. Buchner et al, 1989], [21, The Council of the EU, 1992], [85, EIPPCB, 2004-2005].

3.3.4.11.2 Waste acid neutralisation

Description

Refer to the general description in Section 3.3.4.11 above.

A method applied for strong waste acid is to use lime and/or limestone as a neutralisation agent and to sell white and red gypsum as a co-product or to landfill red gypsum. In order to reduce the landfill volume, alternative routes for red gypsum, are used in the cement industry and for capping and landscaping activities. Only one site uses ammonia as a neutralising agent. Precipitated metal hydroxides are used for landfill or sold as a co-product. Ammonium sulphate is sold as a co-product. A method applied for weak acid is to optimise its re-use in the process or to neutralise it using common and available neutralising agents.

Achieved environmental benefits

The total volume of the spent acid amounts to approximately 6 – 9 tonnes per one tonne of TiO₂ produced. Therefore acid neutralisation has a direct positive impact on the environment.

At the same time, the neutralisation of acid with lime, which leads to the generation of large amounts of solid gypsum, may become an environment friendly option, if only adopted as the long term strategy focused on the maximum utilisation of gypsum to final marketable products, such as white gypsum plasterboards and red gypsum soil conditioners. In case of the neutralisation of spent acid with ammonia, ammonium sulphate fertiliser is then a final marketable product.

Cross-media effects

Substantial amounts of neutralising materials (chalk, lime) to produce white and red gypsum are required. In particular, substantial amounts of the red gypsum may need to be landfilled if its utilisation as a conditioner of local soils exceeds the local demand.

Also, a certain amount of energy is required (see Table 3.54) for the production and handling of white and red gypsum, much less, however, than that required for the concentration and recycling of acid. In the case of the neutralisation of the spent acid with ammonia to produce ammonium sulphate, a long term market demand needs to be confirmed for this nitrogen-sulphate fertiliser.

Another cross-media effect, but only in the case where chalk is used for neutralisation, is the release of CO₂ to the atmosphere.

Operational data

See Table 3.54 and Table 3.55. Refer also to Sections 3.3.4.5 and 3.3.4.7.

In particular, data concerning aqueous emissions, however, covering both acid recycling or neutralisation, are given in Table 3.47. The following are specific loads in the process waste water from the filtration and washing section:

| | | | |
|--------------------|-----------------|---------|-----------|
| • SO ₄ | 30 – 730 kg/t | average | 274 kg/t |
| • Fe | 0 – 158 kg/t | average | 18 kg/t |
| • Cd | 0.001 – 3.2 g/t | average | 0.799 g/t |
| • Hg | 0.000 – 2.2 g/t | average | 0.31 g/t |
| • other metals | 0.001 – 17 kg/t | average | 3 kg/t |
| • suspended solids | 0.09 – 41 kg/t | average | 12 kg/t. |

More characteristic data for this technique, covering only acid neutralisation, are given in Section 3.3.3.6 (Environmental performance – Grimsby Works 2002). In particular, the level of total sulphates in 2002 is reported at 591 kg/t TiO₂ produced.

Waste acid neutralisation is inseparably connected with solid waste generation. This pertains particularly to the amounts of waste to land in the form of white gypsum and red gypsum. However, with a well thought out long term strategy focusing on the utilisation of white gypsum as a co-product for the production of plasterboard, which is then put into operation, the quantities disposed of to land are zero (see Table 3.49).

As can be seen from Table 3.49, the tonnage of red gypsum disposed to landfill in 1999 varied in the range between 1113 – 6918 kg/t TiO₂ produced. In turn, data included in Section 3.3.3.6 (Environmental performance – Grimsby Works 2002), indicate for a possibility to make great progress in the utilisation of red gypsum. Therefore, in some locations where there is strong demand for red gypsum (soil conditioner in blends with organic fertilisers, inert material used for capping and landscaping activities of old quarries, landfills and contaminated sites, and co-product used in the cement industry), the tonnage of red gypsum disposed of to landfill can be substantially reduced or even eliminated. Refer also to Section 3.3.4.11 above.

Applicability

In principle, applicable to all TiO₂ plants using the sulphate process route (refer to the explanations included in Section 3.3.4.11). Waste acid neutralisation is, in principle, an option mutually excluding waste acid recycling (see Section 3.3.4.11.1).

Economics

Refer to data included in Table 3.54 and Table 3.55.

Driving force for implementation

The protection of the environment.

Example plants

Titanium dioxide plant in Grimsby, UK.

Reference literature

[20, CEFIC-TDMA, 2004]; [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [48, W. Buchner et al, 1989], [21, The Council of the EU, 1992], [85, EIPPCB, 2004-2005].

3.3.4.12 Co-products for sale or re-use

Description

Ferrous sulphate, ferric sulphate, iron oxide, and other copperas related products (refer to Section 7.5), as well as white gypsum, red gypsum, and reconcentrated sulphuric acid, are all potential co-products in the manufacturing of titanium dioxide by the sulphate process route. Their production depends mainly on local markets.

The goal to maximise the conversion of potential 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 these co-products, is a proven long term strategy applied across the European titanium dioxide industry. Whatever the recovery system used, the following hierarchy applies:

- avoidance of waste generation with preservation of resources
- reduction of waste generation
- re-use of waste (preferably inside the process or, if this is not possible, then outside of the process)
- waste disposal.

Chapter 3Achieved environmental benefits

Minimisation of wastes, otherwise released to the environment (refer to data included in Table 3.49 and Table 3.50).

Cross-media effects

Often there are local restrictions on markets and it can be counterproductive to transport low cost co-products long distances.

Operational data

No other data submitted apart from these included in the preceding sections. Refer in particular to data included in Section 7.5 on 'Copperas and related products', and to information relevant to white gypsum included in Sections 3.3.3.5.2, 3.3.3.6, 3.3.4.11.2 and Figure 3.6.

Applicability

In principle, applicable to all plants producing TiO₂ by the sulphate process route.

Economics

No detailed data submitted.

Driving force for implementation

Reducing the impact on the environment, among others resulting from the requirements of the TiO₂ Harmonisation Directive [21, The Council of the EU, 1992].

Example plants

The strategy to manufacture co-products for sale or re-use is, to a various degree, characteristic to all fifteen EU-25 titanium dioxide plants based on the sulphate process route (see Table 3.5).

Reference literature

[20, CEFIC-TDMA, 2004], [42, UBA-Germany, 2001], [26, EIPPCB, 2003], [59, CEFIC-TDMA, 2004].

3.3.4.13 Energy usageDescription

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].

In broad terms, acid recycling uses 11.5 GJ/tonne TiO₂ more energy than neutralisation. However, this is only one component in the matrix of factors that must be considered when selecting the mode of effluent treatment.

A technique to consider with regard to energy efficiency is to use pressure filters for the kiln feed. Partly recycling off-gases in the calcination section is used for energy saving in the TiO₂ industry. In order to make use of the off-gas energy, dust removal is essential requiring the use of suitable systems such as electrostatic precipitators at high temperatures.

The use of slag or slag ilmenite mixtures avoids the use of concentration of the liquor prior to precipitation. For product quality reasons, this often is not practical with pure ilmenite feedstock since the hydrolysis conditions are too aggressive to maintain an even floc size distribution in the precipitate. Waste heat from steam condensation is utilised in the process.

As mentioned above, acid recycling increases the total energy consumed at the site by approximately 30 %.

Achieved environmental benefits

Energy efficiency in the process is also an indirect measure of the impact of TiO₂ production on the environment. The less energy used for TiO₂ production, the less energy used in primary fuels and, consequently, the less emissions of CO₂, SO_x, and NO_x to the atmosphere related to the generation of energy used in the process.

Cross-media effects

No data submitted.

Operational data

The range of energy usage in TiO₂ plants operated by the sulphate process route (understood as the overall total energy consumption per site) varies between 23.7 – 45.3 GJ/t TiO₂ produced – refer to Table 3.39 [20, CEFIC-TDMA, 2004]. In turn, the minimum and maximum values of all German production locations are quoted in the range between 32.7 – 40.9 GJ/t TiO₂ produced [42, UBA-Germany, 2001].

It should be also noted that energy usage for acid recycling is reported in the range of 10.2 - 18.0 GJ/t TiO₂, while this, for acid neutralisation is in the range of 0.2 – 6.5 GJ/t TiO₂, the difference between the average figures of energy usage being 13.8 – 2.3 = 11.5 GJ/t TiO₂ produced (refer to Section 3.3.3.2.1).

Applicability

Applicable to all plants producing TiO₂ by the sulphate process route.

Economics

No detailed data submitted. Refer to the LCA study in Section 3.4.5.

Driving force for implementation

Reduced impact on the environment and decreased manufacturing costs of TiO₂ production.

Example plants

Titanium dioxide plant in Grimsby, UK (and the other fourteen European TiO₂ plants based on the sulphate 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].

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3.4 Comparison of the chloride and sulphate processes

3.4.1 Introduction

Ever since the chloride process became a viable production method for the manufacture of titanium dioxide, comparisons have been made from an environmental point of view and from other standpoints. Since the beginning, both processes, and particularly the sulphate process, have undergone radical changes and improvements. These changes were initiated by the enactment of the Titanium Dioxide Harmonisation Directive [21, The Council of the EU, 1992]. More importantly, the change and improvement process has continued ever since, and this has been due to several factors, the most important of them being:

- availability of feedstocks
- introduction of certified environmental management systems such as: ISO 14001 and EMAS, which embrace the commitment to continual environmental improvement.

It is the intention in this section to qualitatively compare and contrast the two processes as they are developed now. Additional comparisons can be made by consulting the performance data in Sections 3.2.3 and 3.3.3 above, and in the process flow sheets (Figure 3.2 and Figure 3.4 above).

It is not intended to carry out a full life cycle assessment of the two processes but reference will be made to such studies where appropriate (see Section 3.4.5 below).

3.4.2 Direct comparison of the chloride and sulphate processes

3.4.2.1 Ore Import

This is a key area, which has changed since the introduction of the chloride process. Both the chloride and sulphate processes can use the same natural feedstock ilmenite (43 – 60 % TiO₂).

However, the use of ilmenite in the chloride process requires specific know-how of how to avoid a large build-up of metal chlorides in the solids separation section and, more importantly in this context, produces large amounts of ferrous chloride, which are difficult to dispose of. There is also a large consumption of chlorine, which can increase the manufacturing cost of TiO₂ pigment production. Currently, only some plants in the US are processing ilmenite and deep wells are used to dispose of the waste chlorides.

In Europe, because of the problems mentioned above, the original feedstock for the chloride process was natural rutile (95 – 96 % TiO₂). However over the last 10 years, rutile has become very scarce worldwide to the extent that it is only used infrequently at present (by one site in Europe). The current replacements are:

- 'synthetic rutile' which is made by leaching ilmenite with dilute HCl. This leaching is carried out at the source site
- titanium slag (85 – 90 % TiO₂) which is made by extraction of the iron from ilmenite ores in a blast furnace, followed, if necessary, by an acidic leaching of impurities like magnesia.

A crude comparison between a chloride site using slag and a sulphate site using ilmenite may conclude that the chloride process potentially generates less waste. However, because of the reasons described above, there is no difference in the amount of potential waste coming from each process using the same ore. The difference is that for the chloride process not all the waste is generated at the TiO₂ manufacturing sites (see Section 3.4.5 below).

For the sulphate process, the choice remains with the selection of the ore: ilmenite against upgraded ores. The life cycle issue here is that the extracted iron is not a waste but neither is the iron sulphate co-product ('copperas') which most modern ilmenite-based plants produce and sell for water treatment, etc. Also, it is noted that slag manufacture is energy intensive, whereas copperas manufacture is not.

The main inference here is that simplistic conclusions cannot be drawn in this area.

Other aspects of feedstock preparation are similar for both processes. In one case, the milling and drying takes place on the source site and in the other it is carried out before feedstock use.

3.4.2.2 Feedstock processing – digestion and chlorination

The basic purpose of this part of the process is similar. It is to liberate the titanium from the strong chemical bonds in which it is held in the feedstock. The sulphate process uses concentrated sulphuric acid at 100 to 200 °C usually reacting over a number of hours in a batch process to maximise yield. The chloride process uses chlorine passed through a fluidised bed of coke and feedstock at ~ 1000 °C.

The main gaseous emissions are CO, COS and CO₂ and occasionally Cl₂ for the chloride process and SO_x and traces of H₂S (if slag is the feedstock) for the sulphate process.

In modern processes, CO and COS are rendered less harmful in thermal oxidisers by conversion to CO₂ and SO₂. Cl₂ is removed by scrubbing. Similarly SO_x and H₂S are substantially reduced by multistage scrubbing.

Both processes are of very high chemical efficiency and overall are exothermic. No solid waste is generated at these stages of the processes.

Both chlorine and concentrated sulphuric acid are hazardous materials, however, chlorine is recognised to require extra special care in its transport, storage and usage. This is acknowledged internationally and the chloride process is subject to the Seveso II Directive [23, The Council of the EU, 1996] for dangerous substances (chlorine and titanium tetrachloride) that require a detailed 'Safety Report' to be prepared for each site as a prerequisite for a licence to operate.

3.4.2.3 Feedstock processing – impurity removal

This section covers:

- solids separation, condensation and gas scrubbing and TiCl₄ purification for the chloride process
- reduction, clarification and crystallisation, hydrolysis filter and wash for the sulphate process.

It should be noted, that because of the radically different nature of the two processes, simple comparisons of the impurity removal in the chloride and sulphate processes are not possible. However, because the primary purpose of the analysed sections is impurity removal, they are considered under this heading.

Table 3.56 exemplifies a comparison of the impurity removal sections of the two processes.

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| SULPHATE | CHLORIDE |
|---|---|
| <p>REDUCTION This is unique to the sulphate process using ilmenite feedstock and its purpose is to convert all the iron to the soluble ferrous form. A small amount of hydrogen is generated. Treated scrap iron is normally used and, if this contains any insoluble matter it must be neutralised and removed as a waste.</p> | There is no equivalent step in the chloride process. |
| <p>CLARIFICATION AND SOLIDS SEPARATION Most of the insoluble impurities are removed and treated at this stage together with unreacted feedstock. The product is neutralised with lime to remove residual sulphuric acid and either disposed of to land as an inert material or, if the opportunity is available, used after further treatment for land restoration in civil engineering projects. No significant atmospheric emissions result from this stage. Solid waste is generated from the impurities in the feedstocks.</p> | <p>SOLIDS SEPARATION As with the sulphate process, most of the impurities (including iron) together with unreacted feedstock, are removed at this stage. The main difference, as compared to the sulphate process, is that it is a vapour phase desublimation rather than an aqueous process. The solids are repulped in water, neutralised with lime and landfilled or, in some cases, converted to saleable products. No significant atmospheric emissions result from this stage.</p> |
| <p>CRYSTALLISATION (ILMENITE ONLY) The majority of the iron is removed here to be used as a co-product as described above. This requires some energy but there are no significant air emissions.</p> | <p>CONDENSATION/GAS SCRUBBING Tetrachloride vapour is condensed and further purified. The gas stream is passed through a thermal oxidiser and then treated in a variety of ways to produce various co-products. Heat from the thermal oxidiser may be recovered or used to maintain buoyancy in the exit gas stream to improve atmospheric dispersion.</p> |
| <p>HYDROLYSIS The purified titanyl sulphate solution is hydrolysed under controlled conditions by seeding and boiling to produce hydrated titanium oxide ('pulp'). Some energy is used as steam.</p> | There is no equivalent step in the chloride process |
| <p>FILTER AND WASH The pulp is first filtered washed and then leached to remove residual impurities. The waste acid solution is sent forward to the effluent treatment plant.</p> | <p>TiCl₄ PURIFICATION The final purification of the tetrachloride is carried out by complexing vanadium with oil in the distillation column. The solid waste is returned to the main solid waste stream and the pure product is sent to storage. Steam energy is used for the distillation.</p> |

Table 3.56: Comparison of the impurity removal sections of the two processes

3.4.2.4 Raw pigment production – calcination and oxidation

Calcination produces aggregated pigment sized crystals from hydrolysed pulp and can also change the crystal habit from anatase to rutile. Oxidation is the burning of pure tetrachloride in oxygen to produce similar pigmentary sized particles, however only rutile can be produced.

Both processes are energy intensive and produce a gas stream as detailed below:

- in the sulphate process, SO_x, dust and water vapour are produced from calcination. In almost all sulphate sites in Europe, the SO_x is catalytically oxidised and converted to sulphuric acid, which, as with the dust, is recycled back into the process
- in the chloride process, chlorine is produced from oxidation, which is then recycled directly or indirectly back to chlorination.

Calcination is an open system operating at atmospheric pressure whereas oxidation must operate in a totally closed system, which, for direct recycling systems, operates above ambient pressure. High integrity, fully operationally reliable systems and procedures are required to prevent any significant chlorine emissions.

3.4.2.5 Raw pigment preparation for finishing

From here on the techniques used in the sulphate and chloride processes are similar, if not the same.

In the sulphate process, calciner discharge is cooled in a conventional open rotary cooler, which allows re-use of the heat, whereas in the chloride process, oxidation reactor discharge requires a closed purpose built cooler to ensure no loss of chlorine. In the chloride process, the reactor discharge is separated from the chlorine by high integrity bag filters.

In the sulphate process, calciner discharge normally needs dry and wet milling to break down large aggregates. This is not required in the chloride process for reactor discharge, but degassing and removal of residual chlorine is necessary. Both products are usually wet milled as well.

3.4.2.6 Finishing

The finishing stage is identical for both processes as described in Section 3.3.2.9 above.

3.4.2.7 Effluent treatment

As is described earlier, the sulphate process liquid effluent is treated in a number of different ways to reduce the environmental impact of that effluent.

For the sulphate process iron salts are extracted for commercial use (reference can be made to Section 7.5 on 'Copperas and related products'), sulphuric acid is reconcentrated for re-use, filter salts are roasted to recover the sulphur values and, where possible, the cinder is used commercially. Alternatively, the effluent is neutralised in a stepwise process producing firstly 'white gypsum' for use in plasterboard manufacture, or in the cement industry, etc. followed by 'red gypsum' (an iron hydroxide calcium sulphate mix), which is used in clay soil treatment and land recovery.

Liquid effluent in the chloride process requires a similar treatment (however on a smaller scale than that of the sulphate process). On the other hand, the liquid effluent, resulting from the upstream production of synthetic rutile from ilmenite, is treated similarly to the sulphate process effluent. Red gypsum is one of the by-products.

In the chloride process route, the main recycling operation is that used for recycling the chlorine gas. Sophisticated high integrity systems are required for safe containment of the chlorine and $TiCl_4$, CO, COS. These usually include the ability to liquefy, store and evaporate both chlorine and tetrachloride. Such systems use energy and sub-zero cooling. Carbon monoxide and carbonyl sulphide are invisible toxic gases that require special precautions for safety reasons.

3.4.2.8 Energy

Using the LCA approach (Section 3.4.5) takes account of the environmental effects from the beneficiation process used for the production of feedstock for the chloride process.

The key issue relating to energy usage in TiO_2 production is the emission of greenhouse gases, mainly carbon dioxide. If the coke consumption in chlorination used as a reducing agent is included, the contribution to the emissions of greenhouse gases for both processes are similar.

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3.4.2.9 Water

The sulphate process consumes significantly more water than the chloride process primarily because washing is the only means of removing residual impurities from the hydrolysed TiO₂ pulp.

3.4.3 Direct comparison – abatement of a titanium dioxide plant

3.4.3.1 Sulphate process route

The sulphate process produces large quantities of waste material including metallic sulphates. The conversion of these materials into useful saleable by-products, leads to the minimisation of the releases to the environment. Therefore, techniques available for the sulphate process route include:

- conversion of ferrous sulphate (raw copperas) to the family of ferrum products used for many applications, including water treatment (see Section 7.5)
- conversion of spent sulphuric acid to white gypsum (for wall boarding) or red gypsum (for agricultural land improvement)
- recycling of dilute acid produced by removal of SO₂ from calciner off-gases.

The sulphate process also produces weak acid, SO_x, NO_x and particulates. In this respect, techniques available for the sulphate route include:

- abatement for SO_x, NO_x and particulates, arising from fuel firing and calcining, as well as removal of particulates from waste gases
- subsequent recovery of the SO₂ generated by the roasting of metal sulphates to make sulphuric acid via the contact process
- recycling the metal oxides produced by roasting to the steel industry
- concentration or regeneration of the spent sulphuric acid for recycling or sale.

3.4.3.2 Chloride process route

Tail-gases from the chlorination stage of the process contain carbon monoxide, carbon dioxide with some hydrogen chloride and chlorine 'slip' from the reaction. Conventional two-stage scrubbing techniques, first with demineralised water to remove the hydrogen chloride and then caustic solution to remove chlorine, are techniques available for the chloride process route. All other vents are typically scrubbed with a solution of caustic soda to remove chlorine and make sodium hypochlorite.

The carbon monoxide generated by oxidation of the coke bed of the chlorinator, requires the thermal conversion of the CO in the tail-gas to CO₂.

It is also practicable to convert metallic chlorides in the waste material to the more inert oxide form, which will have a reduced environmental impact and may have values as a co-product.

3.4.4 Conclusions

This comparison indicates there is a great deal of environmental equivalence between modern chloride and sulphate processes that currently operate in Europe. There are obviously detailed differences, which are hard to directly compare. Refer also to BAT Section 3.5 below.

These conclusions are supported by a Life Cycle Assessment study that was carried out by Tioxide in the mid 1990s [24, Tioxide Group Ltd, 1995]. In the LCA study [25, D.G. Heath, 1996] thirteen titanium dioxide production processes and feedstock options were looked at in detail and four of them, two chloride and two sulphate processes, had very similar overall environmental impacts (refer to Section 3.4.5 below).

3.4.5 Life Cycle Assessment in the titanium dioxide industry

For many years now, the issue of true environmental comparability of the chloride and sulphate processes has been an important topic in the TiO_2 industry, especially when considering feedstocks, overall energy consumption and their associated emissions. It was, therefore, reasonable to include the relevant sections of the LCA study, carried out in 1995 in this document [20, CEFIC-TDMA, 2004].

The purpose of the Life Cycle Assessment (LCA) study was to compare six realistic process options for making titanium dioxide. These are listed in Table 3.60.

Tioxide Group Ltd (now Huntsman Tioxide) has developed LCA since 1990. The study modelled the whole production chain: ore – product – waste. For the TiO_2 pigment, the study boundary was the factory gate. The LCA study focused on comparing typical process options and was modelled as far as comparing emissions, with limitations, however, as actual environmental impacts were not modelled. The study was based on well defined system boundaries and functional units, as well as on reliable and available data, with data gathering and an inventory linked to the real world. A commercial programme, which was peer reviewed, was used in the study.

An integrated approach, adopted in the LCA study to the manufacture of TiO_2 , is illustrated in Figure 3.10.

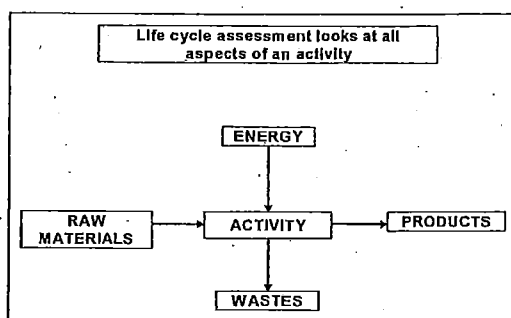


Figure 3.10: Integrated approach in the LCA study on TiO_2 manufacture [20, CEFIC-TDMA, 2004]

The LCA study examined all key inputs and outputs in TiO_2 manufacture, including raw materials, products, utilities and wastes, covering the whole chain of mass/energy balance.

Major assumptions of the LCA inventory study are illustrated in Figure 3.11. Even though the operations of the mining and upgrading of titanium ores were outside the control of Tioxide Group Ltd, emissions relating to these operations and to the transport of ores to the TiO_2 pigment production sites were included in the study. The TiO_2 pigment calcination step was excluded from the chloride route options (as it is not necessary in the chloride process). Finishing operations were assumed to be the same for all examined options, as they are similar in both process routes.

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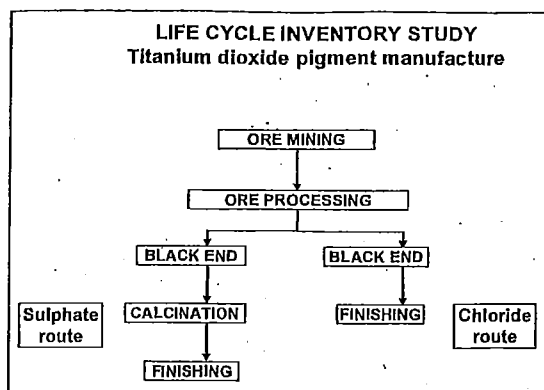


Figure 3.11: Assumptions of the LCA inventory study on TiO_2 manufacture [20, CEFIC-TDMA, 2004]

Mineral feedstock options analysed in the LCA study are presented in Table 3.57.

| MINERAL FEEDSTOCK OPTIONS | |
|---|--|
| <u>Ilmenite and rutile</u> <ul style="list-style-type: none"> beach deposits, mined in Australia, India, etc. physical separation to concentrate required minerals. | <u>Slag and synthetic rutile</u> <ul style="list-style-type: none"> slag <ul style="list-style-type: none"> canadian massive ilmenite smelted to remove Fe, which is sold synthetic Rutile <ul style="list-style-type: none"> Australian ilmenite roasted and leached to remove Fe, which is neutralised and disposed of to land |

Table 3.57: Mineral feedstock options analysed in the LCA study [20, CEFIC-TDMA, 2004]

The analysed sulphate route process options given in Table 3.58 were based on real situations within the Huntsman Tioxide Group.

| | Calais | Huelva | Grimsby | Scarlino | Umbogintwini | Teluk Kalang |
|--------------------------|--------|--------|---------|----------|--------------|--------------|
| Ilmenite | | X | X | | | X |
| Slag | X | | | X | X | |
| Make acid on site | X | | X | | | |
| Purchase acid | | X | | X | X | X |
| Reconcentrate waste acid | X | X | | | | |
| Neutralise waste acid | | | X | X | X | X |

Table 3.58: The sulphate process options considered in the LCA study [20, CEFIC-TDMA, 2004]

Other assumptions of the LCA study are given in Table 3.59.

| OTHER ASSUMPTIONS | |
|--|---|
| <u>Location</u> <ul style="list-style-type: none"> hypothetical plant in north east of UK eliminates transport variables when comparing process options. | <u>Electricity generation</u> <ul style="list-style-type: none"> based on UK generation mix of coal/oil/gas/nuclear implications for SOX emissions. <u>Finishing plant</u> <ul style="list-style-type: none"> common model for all scenarios. |

Table 3.59: Other assumptions of the LCA study on TiO_2 manufacture [20, CEFIC-TDMA, 2004]

Thirteen titanium dioxide production options and different feedstocks were considered in the LCA study, however, the six most typical ones discussed here are listed in Table 3.60. Options A, B, C, and D relate to the sulphate route, while E and F to the chloride route. In the case of sulphate plants, sulphuric acid was assumed to be made locally which gives a steam benefit (this is now not the case). Option A is where sulphate plants were in the mid 1980s – and was treated as a baseline. Option B, D, E and F all meet the minimum environmental performance standards of The TiO₂ Harmonisation Directive 92/112/EEC [21, The Council of the EU, 1992]. Option C is where sulphate plants can be when driven by tighter local regulations that have already been achieved in Italy, Spain and Malaysia.

| Key | Feedstock | Process | Waste treatment |
|-----|------------------|----------|--|
| A | Ilmenite | Sulphate | None |
| B | Ilmenite | Sulphate | EU standard neutralisation (800 kg SO ₄ /t TiO ₂) |
| C | Ilmenite | Sulphate | Full neutralisation (300 kg SO ₄ /t TiO ₂) |
| D | Slag | Sulphate | EU std. acid re-concentration (800 kg SO ₄ /t TiO ₂) |
| E | Slag | Chloride | EU standard neutralisation (450 kg Cl/t TiO ₂) |
| F | Synthetic rutile | Chloride | EU standard neutralisation (228 kg Cl/t TiO ₂) |

Table 3.60: Feedstock process environment options discussed in the LCA study [20, CEFIC-TDMA, 2004]

Gross primary energy demand for the manufacture of the TiO₂ pigment step by step in six examined options is illustrated in Figure 3.12.

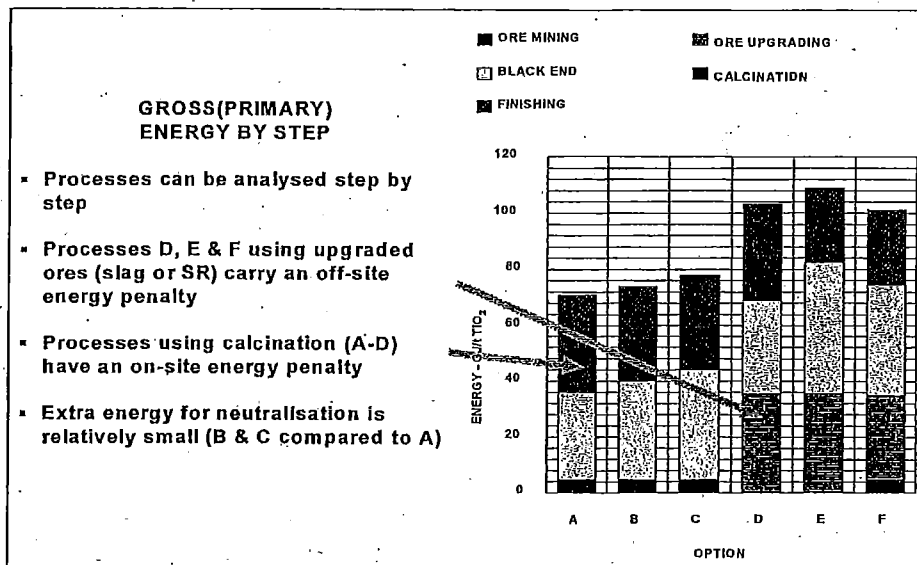


Figure 3.12: Gross primary energy demand for the manufacture of the TiO₂ pigment step by step [20, CEFIC-TDMA, 2004]

Figure 3.12 shows that the overall energy usages for the chloride process (options E and F) have the highest overall energy usage, and even though sulphate plants using the calcination stage pay an energy penalty, the ore upgrading energy penalty is even higher.

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More pigment finishing energy for the chloride process (options E and F) was required in the past as there was no sulphuric acid plant, and therefore, more energy was needed for steam generation (this is now not the case).

Energy consumptions in the preparation of raw materials are included in the totals. Where the preparation involves the production of more than one useful material (as is the case with slag), the environmental burden is shared between the materials in proportion to their perceived commercial value and the unit quantities produced. As far as CO₂ emissions are concerned, they follow the total primary energy usage (with a slight increase for current sulphate plants where sulphuric acid production has ceased).

It should be noted, however, that there have also been changes in the patterns of energy usage in the UK since 1995, which are connected with:

- a switch from LPG and fuel oil to natural gas
- a change to integrated gas fired CHP plants.

As illustrated in Figure 3.13 below, emissions of sulphur oxides (SO_x) examined in five options (from B through to F) as against baseline option A (no SO_x treatment), are lower in the sulphate route options than those in the chloride route options, because of a strong influence of the overall energy demand on SO_x emissions. Also, as assumed in the LCA study, the energy generation scenario typical for the UK – the use of coal and oil, implies higher SO_x emissions in the chloride process route options. In fact, when energy generation is excluded, SO_x emissions both from the chloride and sulphate process routes alone are very low.

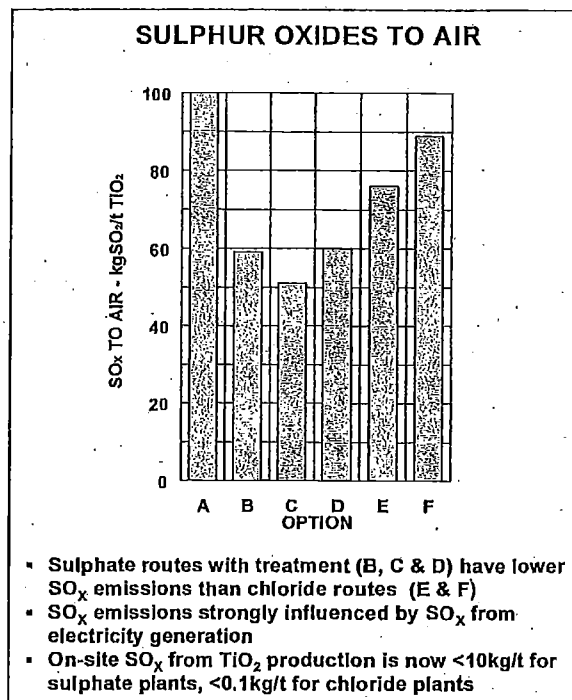


Figure 3.13: Emissions of sulphur oxides to air analysed in the LCA study [20, CEFIC-TDMA, 2004]

In particular, emissions of sulphur oxides have dropped since 1995 in the sulphate process plants because of improved scrubbing of the calcination and digestion gases, and the closure of old sulphuric acid plants (in favour of purchasing high specification smelter acid), and in general, because of the switch of energy source from fuel oil to natural gas.

As illustrated in Figure 3.14, the acidity of the waste liquid streams also fell substantially. Dramatic reduction in acid released to water can be noted in option C (comparable to the chloride process options E and F), when full neutralisation is applied. The acidity level in option D (reconcentration of weak post-hydrolytic sulphuric acid) is higher than that in option B, due to a relative mix of acid and metals in the waste streams.

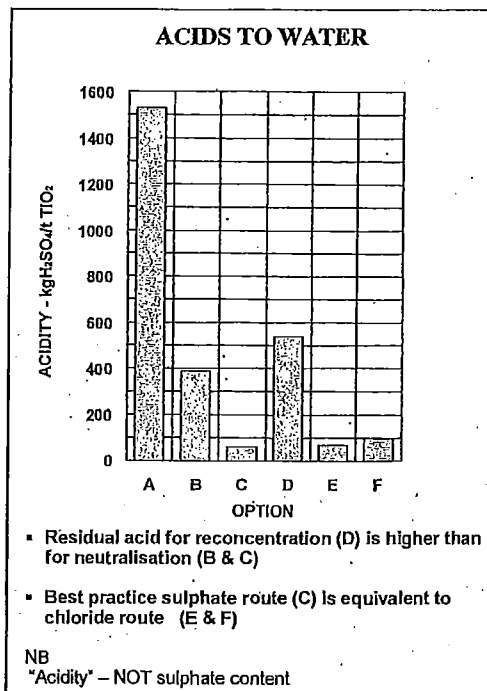


Figure 3.14: Releases of acids to water analysed in the LCA study [20, CEFIC-TDMA, 2004]

In terms of acids released to water from the titanium dioxide plants, the major changes applied since 1995 include:

- full neutralisation of chloride plant acids
- improved neutralisation of sulphate plant wastes.

The amounts of industrial solid wastes generated in the whole chain of operations applicable to the manufacture of titanium dioxide pigments analysed in the LCA study, are illustrated in Figure 3.15.

As compared to the baseline option A (plant not equipped with a neutralisation facility), option D (sulphate process based on slag processing and reconcentration of sulphuric acid) performs best, followed by option E (chloride process based on slag processing). This is obvious, as the treatment of acid yields additional solid residues (in particular, inert gypsum). Option C (sulphate process, ilmenite, full neutralisation) is, therefore, characterised by the highest amount of solid wastes per tonne of TiO₂ pigment produced.

The long term strategy of the utilisation of both co-produced gypsum and copperas-related products (see Section 7.5) is therefore of great importance for reducing the amount of industrial solid wastes generated in the manufacture of titanium dioxide pigments. In option F, solids are generated, in principle, in the beneficiation process.

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The changes in the generation of solid wastes since 1995 are attributable in particular to:

- increased sales of white gypsum (gypsum plaster industry)
- use of red gypsum as a secondary raw material (improvement of soil conditions)
- higher degree of utilisation of copperas and increased sales of iron chemicals, which means that less iron ends up as a constituent of solid wastes.

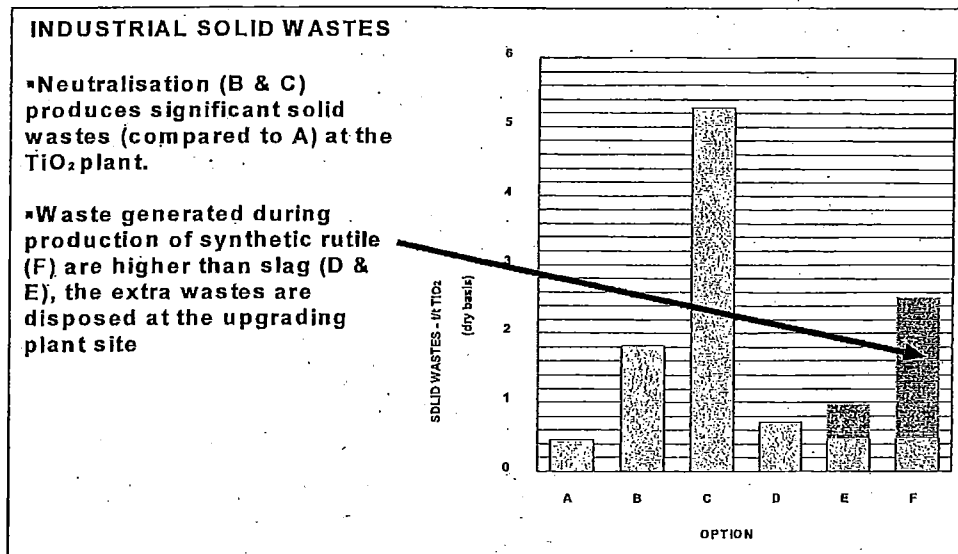


Figure 3.15: Solid wastes generated in the whole chain of operations relating to the TiO_2 industry [20, CEFIC-TDMA, 2004]

The LCA study helped Huntsman Tioxide to clarify environmental concerns in the titanium dioxide industry, and in particular it:

- indicated the potential impacts of process options
- suggested that there is no single 'best' option – in particular the long term availability of a local market for low value co-products is an important factor
- highlighted continuous improvement in performance achieved as part of an overall management system.

The LCA study allowed for ongoing evaluation of environmental concerns in the titanium dioxide industry, including new processes, raw materials, and products, as well as investments in long term co-product development.

The LCA study indicated a potential environmental impact of TiO_2 manufacture, while the EIA programmes quantified the actual impact of the titanium dioxide industry on the environment.

3.5 Best Available Techniques for the production of titanium dioxide

In understanding this section and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: 'How to understand and use this document'. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this section have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the sector, including:
 - environmental requirements and minimum environmental performance standards in the EU stemming from the implementation of the TiO₂ Harmonisation Directive, to which the titanium dioxide industry is required to comply
 - the environmental impact outside of the EU due to upgrading titanium ores prior to the production of titanium dioxide
 - precautions regarding chlorine inventory in the chloride process route, and measures adopted to utilise spent post-hydrolytic sulphuric acid in the sulphate process route
 - substantial energy use involved in both routes, in particular in the sulphate process
- examination of the techniques most relevant to address these key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense, all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible consumption and emission levels associated with the use of BAT, are presented in this section that are considered to be appropriate to the sector as a whole and in many cases reflect the current performance of some installations within the sector. Where emission or consumption levels 'associated with best available techniques' are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The consumption and emission levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of 'levels associated with BAT' described above is to be distinguished from the term 'achievable level' used elsewhere in this document. Where a level is described as 'achievable' using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

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Where available, data concerning costs have been given together with the description of the techniques presented in the previous section. These give a rough indication about the magnitude of the costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this section are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation. In this way they will assist in the determination of appropriate 'BAT-based' conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BAT reference documents do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable consumption and emission levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

As discussed earlier in this document, titanium dioxide is currently produced using two distinct process routes: chloride and sulphate. New TiO₂ plants in the EU are likely to adopt the chloride process route, as it offers better raw material and energy efficiency, along with a more compact plant layout which typically benefits in reduced scope of plant maintenance.

Subject to maintaining low chlorine inventory and measures to reduce the environmental risks associated with chlorine and titanium tetrachloride handling, commensurate with the application of the SEVESO II Directive, the chloride process is preferable from the point of view of overall environmental impact in the EU.

However, given the findings of the Life Cycle Analysis, neither process route is de facto selected as BAT and conclusions for both process routes are presented here in parallel.

For titanium dioxide plants in the EU-25, the following are BAT:

3.5.1 The chloride process route

1. After the basic choice of feedstock has been determined, based on, e.g. life cycle assessment considerations, select and use natural TiO₂ ores or synthetic TiO₂ feedstocks with a TiO₂ content and impurities (including magnesium, calcium, silica, and heavy metals) levels that are cost-effective and that will cause low environmental impacts and efficient use of energy and other non-renewable resources at the TiO₂ plant site – see Sections 3.2.2.1, 3.2.3.2, and 3.2.3.4.1.

The application of this BAT is connected with environmental impacts upstream of the TiO₂ plant site (ore mining and upgrading), therefore, an integrated approach and good industrial practice should be applied in each case of TiO₂ feedstock selection, in order to achieve a high general level of protection of the environment as a whole – refer to Section 3.4.5.

2. Manage supplies, transport, receipt and storage of the TiO₂ ore to maintain a moisture content below 0.3 %, so as to reduce the need for drying of the ore prior to processing – see Section 3.2.4.1.1.

3. Select and use coke with a low sulphur content, as a primary measure to ensure that SO₂ emissions during the normal operation of a plant using an effective off-gas scrubbing system are below 1.7 kg/t TiO₂ pigment – see Sections 3.2.3.4.2, 3.2.3.4.7, 3.2.4.1.3, and 3.2.4.5.
4. Maintain a low chlorine inventory commensurate with application of the SEVESO II Directive – see Section 3.2.4.1.4.
5. Ensure steady state operation of the chlorinator(s) at optimum fluidisation velocity, in order to maintain a high conversion rate of the TiO₂ content in the ore, avoid chlorine slip, carryover of unreacted ore and coke, and build-up of solids in the reactor(s) – see Section 3.2.4.2.
6. Design and operate the chlorination unit allowing for easy and rapid maintenance to minimise unplanned downtime and to avoid uncontrolled emissions – see Section 3.2.4.2.

Possible measures include: the system of water film cooling of the outer surface of the chlorinator shell with the associated temperature monitoring system of chlorinator(s), standby chlorination reactor as an reserve to operating chlorination reactor(s), and the maintenance system allowing for rapid interchangeability between the operational chlorinator being turned off and a standby chlorinator.

7. Ensure that metal chlorides, originating from impurities contained in the ore, are appropriately treated to recover ferrous chloride (FeCl₂) solution from the process, consistent with local market availability, expected ferrous chloride quality and quantity available – see Sections 3.2.4.3 and 7.4.
8. Recover for re-use, the hydrochloric acid, sodium hypochlorite and sulphur from the process off-gas, consistent with local market availability, expected product quality and plant economics – see Sections 3.2.4.5 and 3.2.4.11.
9. For efficient oxidation of TiCl₄ into TiO₂, use a toluene fired furnace or a plasma arc furnace, taking into consideration energy input and the reliability of plant operation, as well as the costs and advantages of each oxidation technique – see Section 3.2.4.7.
10. Design and operate the oxidation and chlorination units in tandem with direct chlorine recycling in the process loop, to achieve low inventory of TiCl₄, minimum chlorine consumption, and low energy usage – see Section 3.2.4.9.
11. Minimise the carryover of the TiO₂ dust from the oxidation system to the chlorine recycling loop, using bag filters or similar, in order to minimise the risk of malfunction in the chlorinator due to solids build-up – see Section 3.2.4.8.
12. Minimise the emission of TiO₂ dust and the discharge of TiO₂ particles in liquid effluents originating from the finishing operations – see Sections 3.2.3.4.8 and 3.2.3.7. Refer also to BAT 14 (1) and 15 (2) below.
13. Improve the overall energy efficiency in the chloride process in the range of 17 – 25 GJ/t TiO₂ pigment (for plants operated at full capacity level), noting that the finishing section consumes majority of the total energy (in the range of 10 – 15 GJ/t TiO₂ pigment), the energy use being highly dependent on the characteristics of the final product. An increase of energy required in the wet treatment and finishing operations is foreseen if customer specifications call for a finer particle size in the final pigment product – see Sections 3.2.3.3.1, 3.2.3.7, 3.2.4.12, 3.3.2.9 and 3.3.3.2.1.

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14. Total emission levels to air associated with the application of BAT, are:

| | |
|----------------------------|--|
| 1) Dust/particulate matter | 0.1 – 0.2 kg/t TiO ₂ pigment |
| 2) SO ₂ | 1.3 – 1.7 kg/t TiO ₂ pigment |
| 3) HCl | 0.03 – 0.1 kg/t TiO ₂ pigment |

15. Total emission levels to water associated with the application of BAT, are:

| | |
|----------------------|--|
| 1) Hydrochloric acid | 10 – 14 kg/t TiO ₂ pigment |
| 2) Chlorides | 38 – 330 kg/t TiO ₂ pigment* |
| 3) Suspended solids | 0.5 – 2.5 kg/t TiO ₂ pigment |
| 4) Iron compounds | 0.01 – 0.6 kg/t TiO ₂ pigment |

(*) For chlorides, the absorption capacity of the receiving water and the raw materials used should be taken into consideration at the local level.

Due to insufficient data reported, no particular techniques associated with the reduction of the emissions of Hg, Cd, V, Zn, Cr, Pb, Ni, Cu, As, Ti and Mn, were identified.

3.5.2 The sulphate process route

1. After the basic choice of feedstock has been determined, based on, e.g. LCA considerations and plant capabilities, select and use TiO₂ feedstocks with as low as practical level of harmful impurities, in order to reduce consumption of raw materials and energy, and reduce waste generation. Both titanium slag and ilmenite can be chosen and used either separately or in blends, on condition that they are cost-effective and that they will cause low environmental impacts and efficient use of energy and other non-renewable resources at the TiO₂ plant site – see Sections 3.3.2.1, 3.3.3.1.1 and 3.3.4.1.

The application of this BAT is connected with environmental impacts upstream of the TiO₂ plant site (ore mining and upgrading), therefore, an integrated approach and good industrial practice should be applied in each case of TiO₂ feedstock selection, in order to achieve a high general level of protection of the environment as a whole – refer to Section 3.4.5.

2. Manage supplies, transport, receipt and storage of the TiO₂ feedstock to maintain a low moisture content so as to prevent the need for drying the feedstock prior to milling and processing – see Section 3.3.4.2.
3. Minimise dust emissions from the handling, drying and milling of the ore, using high integrity bag filters with appropriate filter cloth material and a maintenance routine to control dust losses – see Sections 3.3.3.3.1 and 3.3.4.2. Refer also to BAT 18 (1) below.
4. Mill the ore to an optimum size to maximise the efficiency of digestion – see Section 3.3.4.2.
5. Both batch and continuous digestion of the ore can be used, bearing in mind that continuous digestion is more applicable with ilmenite as a feedstock, and that there is a large amount of expertise within the industry in optimising batch process for maximum efficiency – see Section 3.3.4.3.

6. Treat digester off-gases in order to reduce emissions of sulphur and produce usable sulphur compounds as by-products downstream of the plant site – see Sections 3.3.3.3.2 and 3.3.4.10.1. Refer also to BAT 18 (2) below.
7. For the reduction of ferric ions to ferrous ions in the digester liquor use iron scrap of an appropriate quality to prevent the contamination of the solution with heavy metals like chromium or nickel. The surface of the scrap must be free of dirt, oil, grease, and other contaminants – see Sections 3.3.2.3 and 3.3.4.4.
8. For the processing of ilmenite based feedstocks, apply a batch or continuous system for crystallisation and separation of copperas (iron sulphate heptahydrate) to optimise its removal from the process for downstream uses – see Section 3.3.4.5.
9. For hydrolysis of titanyl sulphate and TiO_2 hydrate precipitation, apply a nuclei producing system, to allow consistent particle size distribution of the calciner discharge – see Section 3.3.4.6.
10. For filtration of the titanium dioxide hydrate from the mother liquor ('strong acid'), use a system which allows the most efficient separation of strong and weak acid, so as to separate the maximum amount of undiluted strong acid from the filter cake prior to its washing – see Section 3.3.4.7.
11. When using acid neutralisation for the utilisation of spent post-hydrolytic ('strong') sulphuric acid, minimise the amount of material sent for disposal by optimising the production of useable gypsum products – see Sections 3.3.3.2.1, 3.3.4.11, 3.3.4.11.2 and 3.3.4.12.
12. Where spent acid is reconcentrated and re-used at the TiO_2 plant site or off site, either for the digestion of titanium ore or the manufacture of other co-products (such as wet phosphoric acid, fertilisers, cement additives), minimise energy consumption for the concentration of sulphuric acid and salt roasting, while reducing the content of the metal sulphates in the concentrated acid to the minimum level, in order not to allow for their build up in the acid recycling loop – see Sections 3.3.3.2.1, 3.3.4.11, 3.3.4.11.1, 3.3.4.12 and 3.3.4.13.
13. Use calcination systems that minimise energy usage without compromising the quality of the TiO_2 pigments, such as pressure filters prior to calcining and hot off-gases recycling on the kilns to save energy – see Sections 3.3.4.7 and 3.3.4.8.
14. For the calciner off-gas treatment, apply the system in which typically dust and SO_2 aerosol are removed by electrostatic precipitators, while the SO_2 component of the gas is catalytically oxidised to SO_3 and absorbed to form sulphuric acid, which is then recycled – see Sections 3.3.3.3.5, 3.3.4.8 and 3.3.4.10.2. Refer also to BAT 18 (2) below.
15. Promote the recovery and production of ferrous sulphate, ferric sulphate, iron oxide, and other copperas related products, as well as reconcentrated sulphuric acid and gypsum, which are all potential co-products in the manufacturing of TiO_2 by the sulphate process – see Section 3.3.4.12.
16. Minimise the emission of TiO_2 dust and the discharge of TiO_2 particles in liquid effluents originating from the finishing operations – see Sections 3.3.3.3.6, 3.3.3.4 and 3.3.4.9. Refer also to BAT 18 (1) and 19 (2) below.

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17. Improve the overall energy efficiency in the sulphate process (for plants operated at full capacity level) in the range of 23 – 41 GJ/t TiO₂ pigment (see Sections 3.3.3.2.1, 3.3.4.11 and 3.3.4.13) and from this:

- 1) 23 – 29 GJ/t TiO₂ pigment in the process with sulphuric acid neutralisation
- 2) 33 – 41 GJ/t TiO₂ pigment in the process with sulphuric acid reconcentration.

Given different combinations of systems used across the EU TiO₂ industry for acid neutralisation and/or acid reconcentration, the extreme ranges as in 1) and 2) above, apply only as indicative levels for the estimation of the overall energy efficiency in the TiO₂ plant in question.

Note also that the finishing section consumes a large share of the total energy (in the range of 10 – 15 GJ/t TiO₂ pigment), and this energy use is highly dependent on the characteristics of the final product. An increase of energy required in the finishing operations is foreseen if customer specifications call for finer particle size in the final pigment product.

Increased sulphate removal from liquid effluent streams requires higher energy usage.

18. Total emission levels to air associated with the application of BAT (for all the possible configurations of the titanium dioxide plant based on sulphate process), are:

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|----------------------------|--|
| 1) Dust/particulate matter | 0.004 – 0.45 kg/t TiO ₂ pigment <5 – 20 mg/Nm ³ |
| 2) SO ₂ | 1.0 – 6.0 kg/t TiO ₂ pigment |
| 3) NO ₂ | monitor NO _x emissions from the calciner* |
| 4) H ₂ S | 0.003 – 0.05 kg/t TiO ₂ pigment |

(*) There is no evidence that any primary measures are used in this industry. NO_x monitoring can help find the basis for future actions.

19. Total emission levels to water associated with the application of BAT (for all the possible configurations of the titanium dioxide plant based on sulphate process), are:

- | | |
|--------------------------|--|
| 1) SO ₄ total | 100 – 550 kg/t TiO ₂ pigment |
| 2) Suspended solids | 1.0 – 40 kg/t TiO ₂ pigment |
| 3) Iron compounds (Fe) | 0.3 – 125 kg/t TiO ₂ pigment |
| 4) Mercury (Hg) | 0.32 mg – 1.5 g/t TiO ₂ pigment |
| 5) Cadmium (Cd) | 1.0 mg – 2.0 g/t TiO ₂ pigment |

Due to insufficient data reported, no BAT AELs were identified for V, Zn, Cr, Pb, Ni, Cu, As, Ti and Mn.