

**ARCHIVES HISTORIQUES
DE LA COMMISSION**

**COLLECTION RELIEE DES
DOCUMENTS "COM"**

COM (75)339

Vol. 1975/0137

Historical Archives of the European Commission

Disclaimer

Conformément au règlement (CEE, Euratom) n° 354/83 du Conseil du 1er février 1983 concernant l'ouverture au public des archives historiques de la Communauté économique européenne et de la Communauté européenne de l'énergie atomique (JO L 43 du 15.2.1983, p. 1), tel que modifié par le règlement (CE, Euratom) n° 1700/2003 du 22 septembre 2003 (JO L 243 du 27.9.2003, p. 1), ce dossier est ouvert au public. Le cas échéant, les documents classifiés présents dans ce dossier ont été déclassifiés conformément à l'article 5 dudit règlement.

In accordance with Council Regulation (EEC, Euratom) No 354/83 of 1 February 1983 concerning the opening to the public of the historical archives of the European Economic Community and the European Atomic Energy Community (OJ L 43, 15.2.1983, p. 1), as amended by Regulation (EC, Euratom) No 1700/2003 of 22 September 2003 (OJ L 243, 27.9.2003, p. 1), this file is open to the public. Where necessary, classified documents in this file have been declassified in conformity with Article 5 of the aforementioned regulation.

In Übereinstimmung mit der Verordnung (EWG, Euratom) Nr. 354/83 des Rates vom 1. Februar 1983 über die Freigabe der historischen Archive der Europäischen Wirtschaftsgemeinschaft und der Europäischen Atomgemeinschaft (ABl. L 43 vom 15.2.1983, S. 1), geändert durch die Verordnung (EG, Euratom) Nr. 1700/2003 vom 22. September 2003 (ABl. L 243 vom 27.9.2003, S. 1), ist diese Datei der Öffentlichkeit zugänglich. Soweit erforderlich, wurden die Verschlussachen in dieser Datei in Übereinstimmung mit Artikel 5 der genannten Verordnung freigegeben.

COMMISSION OF THE EUROPEAN COMMUNITIES

COM(75) 339 final

Brussels, 14 July 1975

Proposal for a

COUNCIL DIRECTIVE

on waste from the titanium dioxide industry

(submitted to the Council by the Commission)

EXPLANATORY MEMORANDUMI. INTRODUCTION

This Directive is based on the principles laid down in the Programme of Action of the European Communities on the Environment of 20 December 1973, OJ No C112, and in particular the principle of "preventing, reducing and, as far as possible, eliminating pollution and nuisances" (Title I page 5).

At present the vast majority of factories manufacturing titanium dioxide (TiO_2) dump their waste at sea or in estuaries, relying on the buffer effect of the sea to neutralize the acid part of the waste and on the capacity of the oxygen present to convert the ferrous sulphate to ferric sulphate, the other waste (various oxides of heavy metals) sinking naturally to the sea bed.

At the same time, it must be realized that the demand for titanium dioxide on the European market is increasing and that the producers hope to double their capacity in ten years, either by extending existing factories or by setting up new ones.

The process generally used in Europe is the "sulphate process"*. To obtain TiO_2 from the commonest ores (ilmenite and slag), these have to be treated with sulphuric acid. Obtaining one tonne of TiO_2 involves 2.6 tonnes of waste, which consists mainly of sulphuric acid and iron sulphate. Assuming that authorization were given for dumping at sea, and also assuming that production were doubled, marine pollution from this waste would be almost bound to double in turn.

A whole series of pollution control campaigns have been conducted at the present dumping grounds; these campaigns have been sponsored by national authorities or sometimes by the producers themselves.

* Chapter 1 of the technical report deals in detail with this section.

It is clear from an analysis of the results of these controls that waste from the TiO_2 industry is potentially or actually harmful. These adverse effects on the marine environment are due above all to acidity, the presence of ferrous sulphate and probably other metals (heavy metals).

The effects in question can take the following various forms, depending on the method and place of dumping:

1. Reduced oxygenation and pH of the water and increased concentration of Fe and heavy metals.
2. a) Temporary shortage of the zooplankton biomass and inducement of effects leading to a deterioration of the morphological structure of its components;
b) repulsion and departure of some species of fish;
c) reduction of the biomass, production and specific diversity of benthic and/or nectobenthic biocenoses in the discharge area. In more severe cases, all animal life may disappear.
3. Change in the colour, transparency and turbidity of the water and temporary reduction of photosynthesis, of phytoplankton and in primary production, particularly in the case of surface dumping. The seabed becomes covered with iron oxides and with oxides of other metals where the dumping is carried out in estuaries and in shallow water.
4. On the other hand, there is no evidence of any toxic effects on man from the consumption of species of fish caught in the dumping areas.

It is therefore advisable gradually to reduce the dumping at sea of this waste over a reasonable and realistic period. Part 1 of the technical report contains an inventory of the waste from the production of TiO_2 . These wastes have been classified in four major categories corresponding to the waste products discharged by factories at different stages of production. These categories are :

- i) insoluble matter remaining after filtration
- ii) "copperas" (ferrous sulphate)
- iii) strong acids
- iv) weak acids or weak liquors

The report also considered how and at what price this waste could be disposed of by either conversion or recycling. It should be borne in mind that the processing cost values date back to the end of 1973 and the beginning of 1974 and must be updated to take account of changes in the economic situation. A study on this is being carried out : it is nevertheless true that the figures given in the report remain fully valid for the purpose of assessing the high cost of treatment in relation to production costs and to allow comparison of the various solutions proposed.

2. COMMENTS ON SOME OF THE ARTICLES AND ANNEXES

The aim of this Directive is gradually to reduce and then to eliminate pollution of the sea by waste from the titanium dioxide industry.

- 1) Several stages are envisaged during the transition period to allow industry to adapt from the present situation to one where ~~there~~ is almost total elimination of dumping at sea.

Stage 1 : 1975 - 1 January 1978

During this period existing and new plants will be able to dump their waste at sea or in estuaries subject to prior authorization (Arts. 4 and 5) and an ecological control of the environment (Art. 7).

Stage 2 : 1 January 1978 - 1 January 1981

Existing plants will have to be equipped with treatment facilities such that "the pollution after treatment is not greater than 70 % of the total untreated pollution"(Art. 8 (3)). These provisions correspond to a 30 % reduction in pollution; the remaining 70 % can be dumped at sea or in

- 1 -

6. 01. 83

estuaries (Arts. 4 and 5 and Art. 8).

New plants will have to be equipped with treatment facilities such that "the pollution after treatment is not greater than 30 % of the total untreated pollution"(Art. 8-2). These requirements represent a 70 % reduction in pollution; the remaining 30 % can be dumped at sea or in estuaries (Arts. 4 and 5 and Art. 8).

This will mean that in the first instance the total pollution is contained and that thereafter it will begin to drop.

Stage 3 : 1 January 1981 - 1 January 1985

Existing plants will have to be equipped with treatment facilities such that "the pollution after treatment does not exceed 30 % of the total untreated pollution"(Art. 8-3 and Annex II). This corresponds to the situation of new plants in Stage 2, where there is a 70 % reduction in pollution, the remaining 30 % being dumped at sea or in estuaries (Arts. 4 and 5 and Art. 8).

The situation for the new plants is the same as in the second stage. This will lead to a significant reduction of the total pollution.

Stage 4 : from 1 January 1985 onwards

Existing and new plants will be required to treat their effluent in such a way that only 5 % of the total untreated pollution remains to be dumped at sea or in estuaries (Arts. 8/2-3 and 9-4).

Total pollution will be reduced by 95 %.

./.

2) There are therefore three aspects to this Directive, namely :

- i) prior authorization
- ii) ecological control of the environment
- iii) the measures which are to be taken to "reduce and eliminate pollution and nuisances".

1. The choice of the dumping area and the waste characteristics must be taken into consideration and the interaction between them must be carefully examined. Thence dumping at sea can only be carried out under certain conditions (Art. 5) and storage on land must meet certain requirements (Art. 6).

2. During the period in which dumping at sea is still being carried out, there must be an ecological control of the environment; marine environment control campaigns will therefore be necessary (Art. 7).

Controls will cover acute toxicity, larval development and bioaccumulation tests in the pelagic chains.

3. Firms in this sector will have to :

- a) store on land the insoluble matter remaining after filtration;
- b) make certain reductions in the total pollution (either 30 %, 70 % or 95 %) Article 8 + Annex II).

These reductions are based on perfectly feasible techniques. With plants using ilmenite, for example, a reduction of 30 % would mean that the ferrous sulphate had been treated, 70 % that the ferrous sulphate and the strong acids had been treated, and 95 % that the ferrous sulphate, strong acids and the bulk of the weak acids had been treated.

3) It should be pointed out that the three and six year periods respectively should enable firms to make the necessary adjustments under realistic economic and technical conditions. (See Part I, para. 2 and 3 of technical document.)

In the case of new plants, construction projects will be able to take account of these requirements (ferrous sulphate and strong acids).

In the case of existing plants, treatment of ferrous sulphate (dehydration + roasting or tipping on prepared spoil heaps) can be carried out during this three-year period. The proposed six-year period should allow these units a choice in the treatment of strong acids. The proposed ten-year period for a 95 % reduction seems to be reasonable for perfecting the treatment of weak acids.

Apart from the fact that this Directive will serve to eliminate almost all marine pollution from this type of waste, its application will encourage waste recycling.

3. LEGAL CONSIDERATIONS

Several Member States have already passed laws on - among other things - the disposal of waste from the titanium dioxide industry.

The German Law of 7 June 1972 on waste disposal requires both local authorities and private individuals to use special plants for the treatment, storage and disposal of solid waste.

Likewise the French Law of 1917 on industrial establishments which are dangerous, insanitary or carry on noisy or noxious trades applies to titanium dioxide manufacturers by virtue of the fact that they process mineral ores using, among other things, sulphuric acid which can cause adverse changes in water (cf No 295 in the nomenclature to this law). The Orders issued by the Préfet pursuant to the abovementioned law authorizing the setting-up of industrial establishments are subject to conditions which govern, among other things, the discharge of effluent into water courses.

A new draft law makes these conditions even stricter and stipulates that any authorization granted must take account of the dangers or drawbacks which the industrial establishment in question may present as regards nature and the environment and must lay down installation and operating conditions concerning, in particular, the purification and disposal of effluent, wastes and residues.

In Italy, it is the Fishing Code (Law 963 of 1965) which applies to discharges at sea.

In the other Member States, general laws on the protection of water, air and soil apply.

The attached proposal for a directive based on Article 100 of the EEC Treaty therefore sets out to harmonize these laws and thus create a coherent set of provisions which can apply in all Member States.

Under Article 100 of the Treaty the Opinion of the European Parliament and the Economic and Social Committee is required.

Proposal for a Council Directive on waste from the
titanium dioxide industry

THE COUNCIL OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community,
and in particular Article 100 thereof;

Having regard to the proposal from the Commission;

Having regard to the Opinion of the European Parliament;

Having regard to the Opinion of the Economic and Social Committee;

Whereas waste from the titanium dioxide industry is liable to be harmful
to human health and to the environment, including aquatic flora and fauna;
whereas it is therefore appropriate gradually to reduce and then to eliminate
pollution caused by the dumping at sea of such wastes;

Whereas the Programme of Action of the European Communities on the
Environment (1) adopted by the Council of the European Communities and
representatives of the Member States meeting in the Council, in the
declaration of 22 November 1973, refers to the need to undertake Community
action against certain types of toxic waste and in particular waste from
the titanium dioxide industry;

Whereas national laws on waste from the titanium oxide industry vary from
one Member State to another; whereas these disparities are likely to
constitute barriers to trade within the Community and will therefore have
a direct effect on the functioning of the Common Market;

Whereas EEC Council Directive No (2) concerns waste disposal in
general; whereas for particularly dangerous waste it is advisable to lay
down a special system offering every guarantee that human health and the
environment is protected against the harmful effects caused by the discharge,

./.

(1) OJ No C 112, 20 December 1973
(2) OJ

dumping or uncontrolled tipping of such wastes; whereas this should be the case with waste from the titanium dioxide industry;

Whereas, in order to attain those objectives there should be machinery for prior authorization of all discharges of waste from the manufacture of titanium dioxide into water courses, lakes and the sea, and for dumping at sea or storage on or in the ground; whereas for industrial establishments located in the territory of a Member State, this authorization must be granted by the competent authority of this State; whereas for industrial establishments located in the territory of a non-member State, the authorization must be issued by the competent authority of the Member State in whose territory the waste is stored or deposited;

Whereas it is also advisable to make the issue of this authorization subject to specific conditions, not only for the dumping of waste at sea or discharge thereof into estuaries but also for storage thereof on or in the soil;

Whereas, to ensure effective monitoring of the marine environment, it is essential that any discharge carried out in a maritime area or an estuary be accompanied by a systematic follow-up on the general ecology of the environment;

Whereas, in order to protect the seas surrounding the Community, it is essential to lay down levels to which discharges of pollutants must be reduced; whereas these levels must be reached in successive stages over a maximum period of ten years from the date of entry into force of the Directive; whereas existing or new industrial establishments and new capacities added to existing industrial premises must use anti-pollution techniques in order to achieve these levels within the required time-limits;

HAS ADOPTED THIS DIRECTIVE :

Article 1

1. The aim of this Directive is the gradual reduction and the elimination from the sea of pollution caused by waste from the titanium dioxide industry.
2. For the purposes of this Directive :
 - (a) "waste" means any residue from the titanium dioxide manufacturing process;
 - (b) "disposal" means the removal, transportation, treatment, recycling or recovery of wastes, the storage and depositing thereof on or in the soil and/or the discharge thereof into water courses, lakes and the sea, and dumping at sea;
 - (c) "existing industrial establishments" means those industrial establishments which have reached their full production capacity before the date of entry into force of this Directive;
 - (d) "new industrial establishments" means those industrial establishments, which are in the course of being set up and which have not reached their full production capacity at the date on which this Directive entered into force, together with all industrial establishments which are set up after this date.

./.

Article 2

Member States shall take the necessary measures to ensure that the waste is disposed of :

- without endangering human health;
- without risk of contamination to water, air or the soil or to the flora and fauna;
- without adversely affecting beauty spots and the countryside.

Article 3

Member States shall take the necessary measures to promote the treatment, recycling and recovery of wastes.

Article 4

The discharge of waste into water courses, lakes and the sea, dumping at sea or storage on or in the ground shall be subject to a prior authorization issued by the competent authority of the State in whose territory the industrial establishment is located.

As regards waste from industrial establishments located in the territory of a non-member State, this authorization shall be issued by the competent authority in the Member State in whose territory these wastes are stored or deposited.

Article 5

1. In the case of dumping at sea or discharge into estuaries, the competent authority shall, on the basis of the information supplied in accordance with Annex 1, grant the authorization referred to in Article 4 on condition that :
 - (a) there is no adverse effect on boating, fishing, leisure activities, ore extraction, desalination, fish and shellfish breeding, on regions of special scientific value and on other legitimate uses of the sea;

- (b) no other means of destruction or disposal exists.
2. Irrespective of the method by which and the extent to which the effluent in question is treated, authorization shall not be granted if the level of dilution is inadequate to ensure that the pH of the receiving water, beyond the actual discharge point, does not exceed the pH value at which acute toxicity is caused.

Article 6

In the case of storage on or in the soil, the authorization referred to in Article 4 shall, irrespective of the method and extent of treatment of the effluent in question, be subject to the following conditions :

- (a) discharge into underground strata is prohibited;
- (b) insoluble substances remaining after filtration shall be stored on land in conditions such that they do not adversely affect the ground water;
- (c) ferrous sulphate treatment products, strong and weak acids and waste other than the insoluble substances remaining after filtration may, if they are not subsequently used, be stored on land provided they do not adversely affect the ground water.

Article 7

1. Irrespective of the method and extent of treatment of the effluent which is to be discharged, any discharge into a maritime area or into an estuary shall be accompanied by a systematic follow-up on the general ecology of the environment.
2. This follow-up shall include in particular :
- (a) an ecological inventory of the current state of the area affected by the releases. This requirement shall be fulfilled when new industrial establishments are set up or when capacity is increased in existing industrial establishments;

- (b) sampling species of molluscs, crustaceans, fish and plankton organisms.

This sampling shall be carried out regularly by a body appointed by the Member State in whose territory the industrial establishment is located. In the case of cross-frontier pollution, the body in question shall be appointed by the Commission.

3. Apart from the monitoring of changes in the marine environment, tests for acute toxicity shall be carried out regularly on species of mollusc, crustacean, fish and plankton which are commonly found in the release area. Over a period of 36 hours, and at an effluent dilution of 1/5000, these tests shall not, for 80 % of the species tested, give rise to mortality. The tests shall be supplemented by tests on larval development, which shall ensure total survival of the larvae after 24 hours at an effluent dilution of 1/5000.
4. When these checks have been completed, discharge operations shall be suspended if :
 - (a) an examination of the general ecology of the area reveals a marked deterioration of that ecology;
 - (b) tests for toxicity induced by the accumulation of metals in food chains indicate an accumulation hazardous to human health;
 - (c) the results of the tests for acute toxicity are at variance with the values set out above.

Article 8

1. Member States shall take the necessary measures to ensure that existing and new industrial establishments are equipped with effluent treatment plant.
2. As from 1 January 1978 the total pollution after treatment from new industrial establishments shall be less than 30 % of the total untreated pollution, and as from 1 January 1985 it shall be less than 5 %.

./.

3. As from 1 January 1978, total pollution after treatment from existing industrial establishments shall be less than 70 % of the total untreated pollution; as from 1 January 1981, it shall be less than 30 % and as from 1 January 1985 it shall be less than 5 %.
4. This total untreated pollution shall, in accordance with Annex II, be defined by pollution category and by the type of ore used.

Article 9

Existing industrial establishments which increase their production capacity after the date of entry into force of this Directive shall be required either to :

- (a) comply with the requirements of Article 8(2) as to the proportion corresponding to the increase in production, and of Article 8(3) as to the proportion corresponding to the former production, on the dates on which each of these requirements enters into force;
or to :
- (b) apply general treatment in both existing and new establishments so that the total pollution after treatment does not exceed the sum of the

Article 10

Member States may adopt stricter regulations without prejudice to the provisions of this Directive.

Article 11

Annexes I and II shall form an integral part of this Directive.

Article 12

Member States shall put into force the measures needed in order to comply with this Directive within a maximum period of eighteen months of its notification and shall forthwith inform the Commission thereof.

Member States shall ensure that the texts of the provisions of national law which they adopt in the field covered by this Directive are communicated to the Commission.

Article 13

This Directive is addressed to the Member States.

A N N E X 1

Provisions governing the dumping* of waste at sea and discharging into estuaries.

1. Waste characteristics

- (a) Quantity and composition;
- (b) Quantity of substances and materials which are to be dumped or discharged daily (weekly, monthly);
- (c) Form in which the waste is to be dumped or discharged, i.e., solid, semi-solid, liquid;
- (d) Physical properties (in particular solubility and density), chemical properties, biochemical properties (oxygen demand, nutritional value) and biological properties (presence of viruses, bacteria, yeast, parasites, etc.);
- (e) Toxicity;
- (f) Persistency;
- (g) Accumulation in the biological matter or sediment;
- (h) Chemical and physical changes occurring in the waste after discharge, in particular the formation of new compounds;
- (i) Probability of any changes which would decrease the marketing potential of nature resources (fish, molluscs, etc.).

2. Characteristics of the dumping or discharge area and methods employed

- (a) Geographical situation, depth of water and distance from the coast;
- (b) Location in relation to living creatures in the adult or growing stage;
- (c) Location in relation to amenity areas;
- (d) Where appropriate, methods of packaging;
- (e) Initial dilution level achieved by the proposed discharge method;
- (f) Dispersion, horizontal displacement and vertical mixing characteristics;
- (g) Existence and effects of current and previous discharging and dumping in the area (including accumulation effects).

* Within the meaning of the London Convention on the dumping of waste at sea.

ANNEX 2

Untreated waste from the sulphate process
 (calculated per tonne of TiO₂ manufactured and
 expressed in kilogrammes)

		Norwegian Ilmenites	Australian Ilmenites	Canadian Slog	Enriched Ore
Category I Pollution	SO ₄ Ions (acid)	4,250	3,170	2,830	2,330
	Iron cations*	+ 920	+ 680	+ 170	+ 55
	Total	<i>H</i> 5,200	3,850	3,000	<i>H</i> 2,400
Category 2 Pollution	Other metal cations	110	100	200	120

* Allowing for additions during manufacture.

ANNEX 2 (continued)

Untreated waste from the sulphate process
(calculated per tonne of TiO₂ manufactured and
expressed in kilogrammes)

	Chlorine used (1)	Natural Rutile 1,360	Synthetic Rutile 1,860	Australian Ilmenites 2,500 - 2,800
Category I Pollution	Cl Ions (acidity) + Iron ⁽²⁾	70 + 1	55 + 25	970 to 680 + 450
	<hr/> Total	<hr/> #/ 70	<hr/> 80	<hr/> # 1,300
Category 2 Pollution	Other metal cations	16	25	35

(1) Values inserted here for record only.

(2) Allowing for additions during manufacture.

The pollution categories affected by the reductions required under Articles 8 and 9 are as follows :

Category 1 : pollution by direct toxicity

- SO₄ ions, acidity (sulphuric acid process)
- CL ions acidity (chlorine process)
- Fe cations (both processes)

Category 2 : pollution by indirect toxicity

- cations of metals other than iron (Ti, Cr, V, Ni, etc.)
(both processes).

POLLUTION CAUSED BY THE TITANIUM DIOXYDE INDUSTRY

TECHNICAL REPORT

POLLUTION CAUSED BY THE TITANIUM DIOXIDE INDUSTRY

TECHNICAL REPORT

<u>General</u>	p. 2
<u>Part 1 - The TiO₂ industry</u>	
CHAPTER I : THE PROPERTIES AND USES OF TiO ₂	p. 3
1) Pigmentary properties	
2) Uses	p. 4
3) Economic situation	p. 5
CHAPTER II : THE PROCESSES	p. 6
CHAPTER III : THE RAW MATERIALS	p. 7
CHAPTER IV : WASTE FROM THE PRODUCTION OF TiO ₂	p. 8
I. GENERAL	p. 8
II. SULPHATE PROCESS	p. 11
1) Waste products inherent in the process	
2) Elimination or treatment of the waste products inherent in the process	p. 21
1. Definition	
2. List of the main means of elimination and treatment that can be envisaged for "waste products inherent in the process"	p. 21
3. Treatment procedure and final waste products	p. 25
A. AHS	p. 25
B. BASIC DATA	p. 26
C. COST ASSESSMENT	p. 28
D. RECAPITULATION	p. 30
III. CHLORINE PROCESS	p. 33
Waste products inherent in the process	
1. General	
2. A. Waste products corresponding to natural rutile ore	p. 35
B. Waste products corresponding to synthetic rutile ore	p. 36
C. Waste products corresponding to Australian ilmenite ore	p. 37
3. Treatments	p. 38
A. Effluents considered	p. 38
B. Main processes	p. 39

Part 2 - Ecological aspects

CHAPTER V : ESTIMATE OF THE PHYSICO-CHEMICAL CHANGES DUE TO DISCHARGES	p. 42
CHAPTER VI : STUDY OF THE BIOLOGICAL EFFECTS OF DISCHARGES	p. 49
The different aspects of the problem	
SECTION I. THE SHORT-TERM EFFECTS	p. 50
1) Data on the behaviour of the marine flora and fauna in the vicinity of the discharges	p. 50
2) Experimental data on their behaviour at different concentrations of the effluent	
Determination of acute toxicity thresholds	p. 53
Results	p. 57
3) Estimate of the direct consequences of the discharges on marine flora and fauna	p. 60
SECTION II. THE LONG-TERM EFFECTS	p. 63
1) The "natural" accumulation process	p. 63
2) Studies of accumulation and induced toxicity carried out in laboratories	p. 66
3) Observations of heavy-metal contents of the marine organisms collected in the discharge area	p. 69
SECTION III. CONCLUSION	p. 72
CONCLUSIONS	p. 74

PART 1

THE TITANIUM DIOXIDE INDUSTRY

GENERAL

The modern world needs a number of manufactured products in order to provide every citizen with a certain standard and quality of life.

The way in which these various products are obtained at the industrial level can be summarized by the following equation:

Raw material + materials used for processing + energy
= product + waste (solid, liquid or gaseous).

One thing is therefore obvious: everything that is put in at the beginning is still there at the end.

In the case of certain industries, the greater part of the original materials is processed and little waste appears in the production chain (the petrochemical industry, for instance). In other industries, however, the raw material is relatively poor in basic constituents of the finished product, and the amount of material contributed for the processing of the raw material is considerable.

This is true of the titanium-oxide-producing industry. One tonne of TiO_2 involves about 2.6 t of waste in the most widely used process, not counting the consumption of water.

CHAPTER 1 - THE PROPERTIES AND USES OF TiO₂

1) Pigmentary properties

Titanium dioxide is at present regarded as the best white pigment. The main properties which help to give it this superiority are examined below.

It should be noted that the two commercial forms of this pigment, "anatase" and "rutile", correspond to two crystalline forms of titanium dioxide. The same names are used to designate the similar crystalline forms which are to be found in nature with a lower degree of purity.

The essential quality of a pigment is its opacity, that is, its power of reflection when dispersed in a medium.

This light-reflecting power is due to the reflection of light at the crystal-medium interfaces. This power will depend on the refractive index of the crystal and, for a given pigment concentration, on the number of crystal facets.

The former value is inherent in the crystal, while the latter is improved by very small crystal sizes, which must however be greater than a minimum size connected with the wavelength of the light to be reflected.

Titanium dioxide

- which has the highest refractive index of all traditional pigments (average index of synthetic rutile for a wavelength of 450 nm : 2.921);
- of which crystals of optimum size (0.05 - 1.5 μ) can be produced synthetically;
- which has very good transparency in the visible range

is therefore a very effective pigment.

Rutile and anatase differ by their behaviour in the ultra-violet range. This behaviour produces differences in the light-fastness of the paints in which they are used.

Lastly it should be noted that coatings of metal oxide make it possible to improve the wettability and dispersibility of the pigments and thus to enhance the quality of the dispersions.

2) Uses

The fundamental characteristics of rutile and anatase crystals have been noted. These properties have led to very widespread use of titanium dioxide in many fields.

Major categories worthy of mention are: (1)

- paints and varnishes	50%
- papers	20%
- plastics	10%
- rubber	4.5%
- floor coverings	4%
- inks	2.5%
- ceramics	2.5%
- synthetic fibres	1.2%
- miscellaneous, including cosmetics and pharmaceutical products	5.3%

Consumption of this pigment, owing to its field of application, may be regarded as an index of a country's degree of industrial development.

With regard to the distribution of its application by sectors, this may vary from country to country, but it should in any case be noted that paints and varnishes represent more than half of total consumption, while the other sectors represent proportions ranging from 3 to 15% of the total.

In all these applications, titanium dioxide is a suspension in the various media.

(1) The distribution of uses shown corresponds to the situation in the United States. This distribution is taken from the study EPA-230/1-73-015 dating from 1973.

3) Economic situation

It is obvious that the future of titanium dioxide is bound up with the development of its traditional fields of application. The effects of competition from similar products are slight in these fields.

The average annual growth in world consumption of titanium dioxide was estimated in 1974 at about 5%. This rate may, however, be expected to increase in the next few years.

By the end of 1974 this substantial demand had led to a rise in prices, which were around 595 units of account (U.A.) per tonne of anatase and 720 U.A. per tonne of rutile (mid-December 1974 prices per consignment of 20 tonnes).

The prices of Japanese products are the highest, followed by European prices, except for those in France and Great Britain, which were subject to taxation as from 1st July 1974. Lastly, American prices appear to be lower.

Countries	USA	BELGIUM	FRANCE	FED. REP. of GERMANY	NETHER- LANDS	ITALY	G.B.
Prices not including tax 20 t consignments	UA/kg	UA/kg	UA/kg	UA/kg	UA/kg	UA/kg	UA/kg
July 1974 Anatase	0.458	0.570	0.333	0.432	0.561	0.585	0.380
Rutile	0.500	0.576	0.580	0.674	0.671	0.713	0.424

The July 1974 prices in UA/kg are based on quotations on 16th July 1974, assuming that one UA = 50 Belgian francs, as given by "European Chemical News", Vol. 25 No. 642.

CHAPTER II - PROCESSES

Description of processes

The method of manufacturing titanium dioxide pigments consists of preparing a titanium dioxide of very high purity from an ore which already contains it, but mixed with other elements.

There is no industrial process for the preparation of titanium dioxide which enables it to be extracted selectively.

Actually the only two existing industrial processes consist of an attack on the whole of the ore followed by selective operations to extract the titanium compound. A final stage enables the titanium dioxide to be obtained from the intermediate compound.

These two methods are the so-called "sulphate" and "chlorine" processes.

In the case of the sulphate process the whole of the ore is attacked by sulphuric acid, and then titanium hydroxide is selectively precipitated. Finally titanium dioxide is obtained by calcination of the hydroxide.

In the case of the chlorine process the whole of the ore is chlorinated and the titanium tetrachloride formed is first of all separated from the other chlorides by mechanical means and then distilled. Finally the titanium dioxide is obtained by oxidation of the titanium tetrachloride. (The chlorine process is generally used only with ores which are rich in titanium (rutile). Only one firm has succeeded in applying this process to poorer ores (ilmenite).)

CHAPTER III - THE RAW MATERIALS

All titanium dioxide is prepared from natural ore. The titanium is contained in the latter mainly in the form of iron titanate in the case of the more ordinary ores (ilmenite) and already in the form of crystallised TiO_2 (rutile form) in the richer ores.

While reserves of ore of the rutile type are small and becoming exhausted, reserves of ordinary ores such as ilmenite are extremely large. In particular, there are enormous deposits of them in Canada and Norway.

As a whole, ore availability should not create any problems during the next 75 years. However, a very great research and development effort is at present being made for the preparation of an ore very rich in TiO_2 (synthetic rutile) from the ilmenite-type ore, in view of the environmental problems created by ores of the ilmenite type.

CHAPTER IV - WASTE FROM THE PRODUCTION OF TiO₂

SECTION I. GENERAL

In this chapter, two categories of "waste" will be discussed:

- a) the waste products inherent in the process, resulting from the carrying out of the production process, that is, from the various separations taking place in the process itself before any treatment;
- b) the final waste products, which are obtained after elimination or treatment of the process waste products. These final waste products may be identical to the process waste products if the factory does not carry out any elimination or treatment. But, by definition, "elimination or treatment of process waste products" is regarded as embracing any intervention which leads to a change in their characteristics, which can range from mere dilution in order to reduce their concentration to very elaborate operations which radically change the nature of the waste.

Before going into this question of waste products in more detail, it is interesting to note that the production of the "TiO₂" pigment industry is very simple to define, because it consists of high-purity titanium dioxide. In all evaluations, the particular additives which enable the performance of the pigments to be improved, and also the residual quantities of impurities, which are extremely small, will be disregarded.

As production consists only of titanium dioxide, all raw materials other than titanium dioxide will of necessity be discarded at one of the stages of the process. Moreover, as production of titanium dioxide is carried out with a certain yield, there will also be some titanium dioxide in the waste products.

That is why, in Section II, for the sulphate process, four cases of production of TiO₂ based on the following ores are considered:

- Norwegian ilmenite
- Australian ilmenite
- Canadian slag
- Enriched ore (hypothetical) containing about 20% of TiO_2
(maximum possible for sulphate process).

Similarly, in Section III, for the chlorine process, three cases of production based on the following ores are considered:

- natural rutile
- synthetic rutile
- ilmenite (hypothetical).

For each of these types of production, account will be taken

- of the quantities of raw materials employed;
- of the total weights of waste products corresponding to these raw materials;
- of the main categories of waste products, stating their nature and quantity.

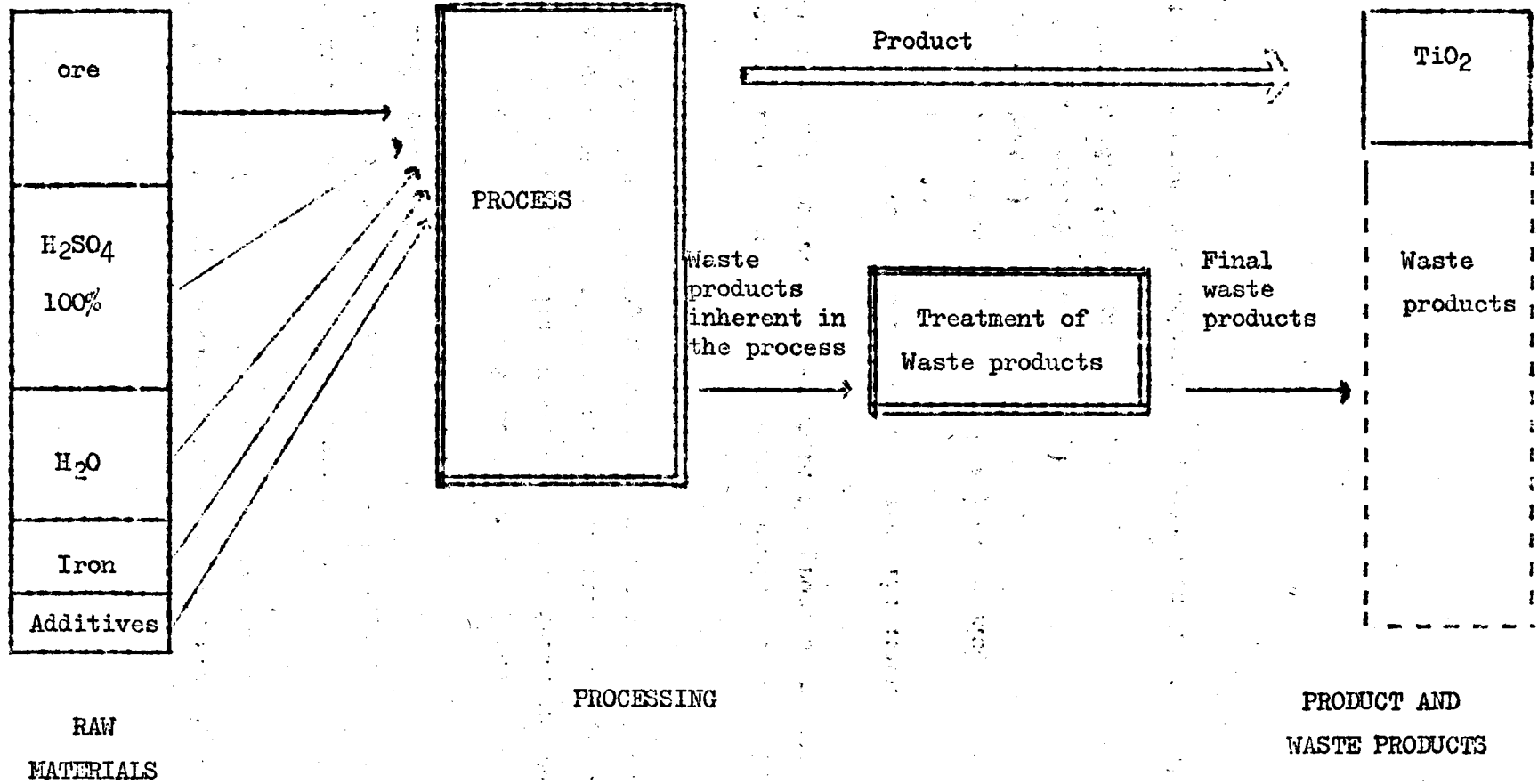
We shall thus see how the various original constituents are distributed in the main process waste products.

PROCESS DIAGRAM

ENV/47/75-E
Orig.: F

- 10 -

Table 1



SECTION II. SULPHATE PROCESS

1) Waste products inherent in process

General

It should not be the purpose of the calculations presented in this chapter to ascertain the exact compositions of effluents.

The reason why such a calculation has nevertheless been attempted is rather in order to achieve a coherent overall analysis based on well-defined hypotheses.

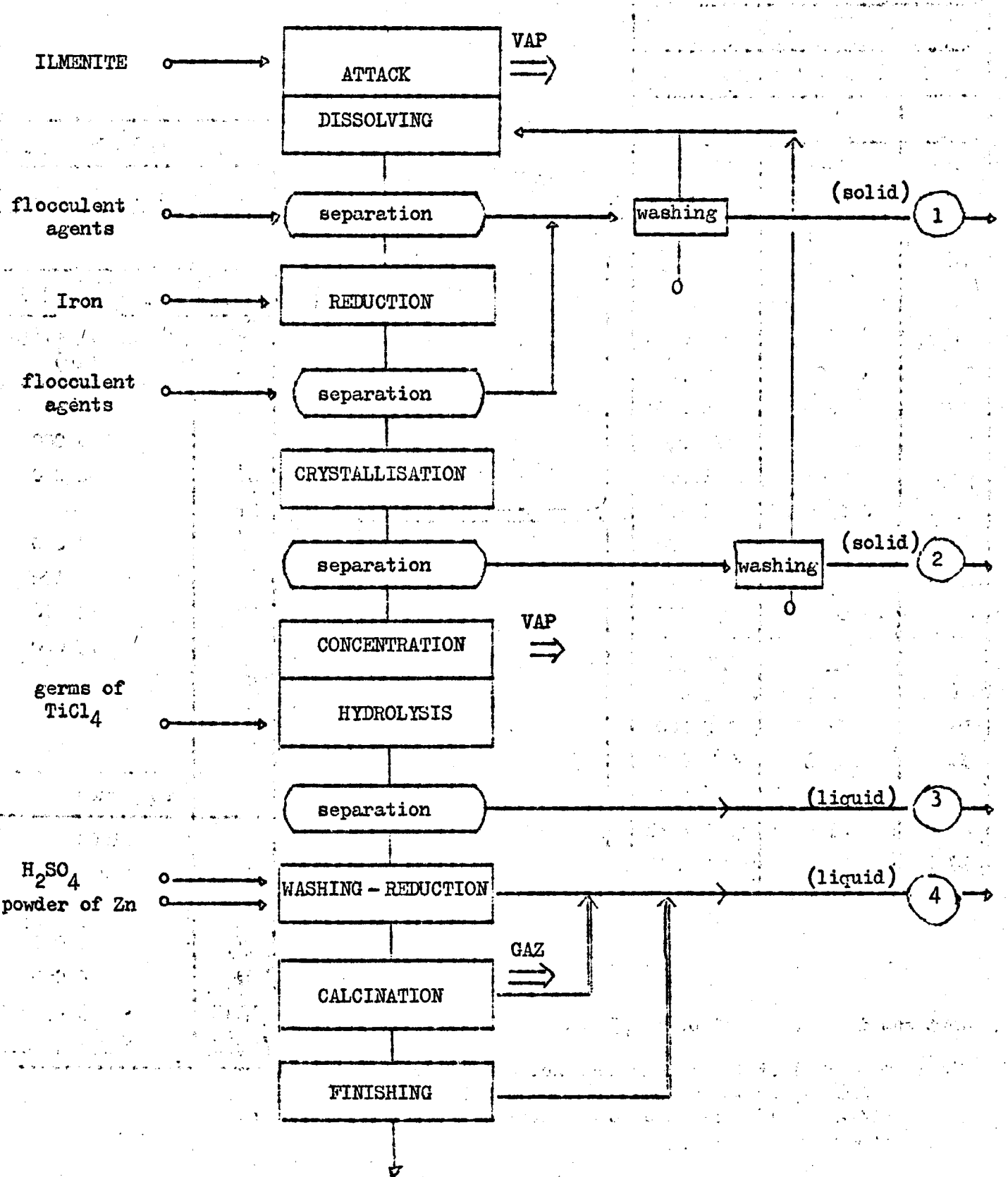
These hypotheses can be argued about and the calculations adjusted, but they do make possible, as far as the main waste products are concerned, a valid quantitative approach for the different types of production and different factory capacities representing the main European producers.

Four main categories of waste products corresponding to possible groupings of the waste products inherent in the process are considered:

- the insoluble substances remaining after filtration
(waste product 1)
- the "copperas" (i.e. ferrous sulphate) compounds
(waste product 2)
- the "strong acids" (waste product 3)
- the "weak acids" (waste product 4)

obtained after the operations schematically shown in the following illustration (Table 2).

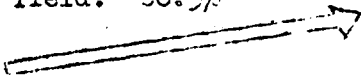
TiO₂ - SULFATE PROCESS (ILMENITE)



WASTE PRODUCTS CORRESPONDING TO ORE A. NORWEGIAN ILMENITE

ORIGINAL ORE		
NORWEGIAN ILMENITE		
	%	kg
TiO ₂	44-45	1130.000
FeO	33-34	827.500
FeO ₂ O ₃	12-13	312.500
SiO ₂	2.5-3.0	68.700
ZrO ₂	-	-
Al ₂ O ₃	0.6-0.7	15.000
P ₂ O ₅	< 0.03	0.700
MnO	2-0.3	5.000
MgO	4.5-5.5	125.000
Cr ₂ O ₃	0.07	1.700
V ₂ O ₅	0.15-0.17	4.000
CaO	0.2-0.3	6.200
Na ₂ O	-	-
S	< 0.04	< 1.000
<hr/>		
	p.p.m.	Grammes
Ni	31-113	253.000
Zn	57-93	187.000
Cu	6-3.2	< 18.000
Cd	< 3-1.9	< 4.000
Pb, Be	< 1	< 2.3 each
Sb, Hg	< 1	< 2.5 each

Yield: 28.5%



PRODUCT
TiO ₂ : 1 tonne

Waste products



FATAL WASTE PRODUCTS	
expressed as quantities of metal (kg)	
Ti	78.000
Fe	756.000
Si	32.000
Zr	-
Al	4.000
P	0.142
Mn	3.870
Mg	75.000
Cr	0.559
V	1.050
Ca	4.275
<hr/>	
in grammes	
S	< 1000
Ni	253.000
Zn	187.000
Cu	18.000
Cd	4.000
Pb, Be	< 2.5 each
Sb, Hg	< 7.9 each

Corresponding weight of ore: 2,500 kg

N.B.: The total of the column does not correspond to 2,500 kg, as the weights of each constituent have average values related to different compositions of ilmenite.

... the ... in this table ...

NORWEGIAN ILMENITE

The quantities shown below relate to 1 tonne of finished product and are based on the values in the preceding table.

Waste product 1 - Insoluble substances

	81 kg	(SiO ₂ , TiO ₂ , Al ₂ O ₃ , MgO, Cr ₂ O ₃ , P ₂ O ₅ , MnO, V ₂ O ₅ , CaO, Si, Ni, Zn, Cu, Cd, Be, Sb, Hg)
+	<u>81 kg</u>	H ₂ O (assuming H ₂ O = 50% of total weight)
	162 kg	

Waste product 2 - Copperas

	3,372 kg	various sulphates, including 2,941 kg FeSO ₄ · 7H ₂ O
+	460 kg	H ₂ O
+	<u>23 kg</u>	free H ₂ SO ₄
	3,855 kg	

Waste product 3 - Strong acid

	727 kg	various sulphates, including 585 kg of FeSO ₄
+	34 kg	TiO ₂ in suspension
+	41 kg	TiO ₂ in solution
+	1,482 kg	H ₂ SO ₄ (exp. as 100%) concentration 20%
+	<u>5,127 kg</u>	H ₂ O
	7,411 kg	

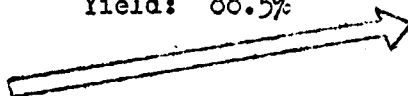
Waste product 4 - Weak acid

	391 kg	various sulphates, including 315 kg of FeSO ₄
+	28 kg	TiO ₂ in suspension
+	22 kg	TiO ₂ in solution
+	300 kg	H ₂ SO ₄ (exp. as 100%) concentration 10%
+	<u>5,753 kg</u>	H ₂ O
	6,000 kg	

WASTE PRODUCTS CORRESPONDING TO ORE B. AUSTRALIAN ILMENITE

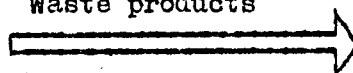
ORIGINAL ORE		
AUSTRALIAN ILMENITE		
	%	kg
TiO ₂	55.4	1130.000
FeO	23.8	485.450
Fe ₂ O ₃	16.9	344.800
SiO ₂	0.15	3.060
ZrO ₂	-	-
Al ₂ O ₃	0.94	19.200
P ₂ O ₅	0.08	1.650
MnO	0.72	14.700
MgO	0.27	5.500
Cr ₂ O ₃	0.14	2.850
V ₂ O ₅	0.17	3.500
CaO	0.02	0.400
Na ₂ O	-	-
K ₂ O	-	-
S	0.01	0.200
Ni	-	-
Zn	-	-
Cu	-	-
Cd	-	-
Pb, Be	-	-
Sb, Hg	-	-

Yield: 88.5%



PRODUCT
TiO ₂ : 1 tonne

Waste products



FATAL WASTE PRODUCTS	
Expressed as quantities of metal (kg)	
Ti	78.000
Fe	498.000
Si	1.400
Zr	-
Al	5.080
F	0.330
Mn	11.370
Mg	3.300
Cr	0.940
V	0.920
Ca	0.280
S	0.200
Ni	-
Zn	-
Cu	-
Cd	-
Pb, Be	-

Corresponding weight of ore: 2,040 kg.

N.B.: The total of the column does not correspond to 2,040 kg, as the weights of each constituent have average values related to different compositions of ilmenite.

Nevertheless, the complex information in this table makes it possible to assess the overall quality and quantity of the waste products.

AUSTRALIAN ILMENITE

The quantities shown below relate to 1 tonne of finished product and are based on the values in the preceding table.

Waste product 1 - Insoluble substances

	20 kg	(SiO ₂ , TiO ₂ , Al ₂ O ₃ , MgO, Cr ₂ O ₃ , P ₂ O ₅ , MnO, V ₂ O ₅ , CaO, Si, Ni, Zn, Cu, Cd, Be, Sb, Hg)
+	20 kg	H ₂ O (assuming H ₂ O = 50% of total weight)
	<hr/>	
	40 kg	

Waste product 2 - Copperas

	1,768 kg	various sulphates, including 1,725 kg FeSO ₄ · 7H ₂ O
+	241 kg	H ₂ O
+	12 kg	free H ₂ SO ₄
	<hr/>	
	2,021 kg	

Waste product 3 - Strong acid

	637 kg	various sulphates, including 584 kg of FeSO ₄
+	34 kg	TiO ₂ in suspension
+	38 kg	TiO ₂ in solution
+	1,250 kg	H ₂ SO ₄ (exp. as 100%) concentration 20%
+	4,291 kg	H ₂ O
	<hr/>	
	6,250 kg	

Waste product 4 - Weak acid

	343 kg	various sulphates, including 314 kg of FeSO ₄
+	28 kg	TiO ₂ in suspension
+	21 kg	TiO ₂ in solution
+	672 kg	H ₂ SO ₄ (exp. as 100%) concentration 10%
+	5,663 kg	H ₂ O
	<hr/>	
	6,727 kg	

WASTE PRODUCTS CORRESPONDING TO ORE C. CANADIAN SLAG

ORIGINAL ORE		
CANADIAN SLAG		
Chemical	%	kg
TiO ₂	70,72	1130,000
FeO	12,15	194,138
Fe ₂ O ₃	1,50	23,960
SiO ₂	3,5-5,0	67,100
ZrO ₂	-	-
Al ₂ O ₃	4,0-6,0	79,890
P ₂ O ₅	0,025	0,399
MnO	0,2	3,195
MgO	4,5-5,5	79,892
Cr ₂ O ₃	0,25	3,994
V ₂ O ₅	0,5-0,6	8,788
CaO	1,2	19,174
Na ₂ O	-	-
K ₂ O	-	-
S	0,05	0,798
NiO	0,085	1,358
Zn	-	1,1
CuO	0,015	0,239
Cd	-	-
Pb, Be	-	0,07
Sb, Hg	-	-

Yield 88,5%

PRODUCT
TiO ₂ : 1 tonne

FATAL WASTE PRODUCTS	
Expressed as quantities of metal (kg)	
Ti	78,000
Fe	159,751
Si	31,3
Zr	-
Al	21,14
P	0,081
In	2,472
Mg	47,935
Cr	1,314
V	2,33
Ca	13,210
Na	-
S	0,798
Ni	1,068
Zn	(1,1)
Cu	0,189
Pb	(0,07)

Waste Products

Corresponding weight of ore: 1,600 kg.

N.B.: The total of the column does not correspond to 1,600 kg, as the weights of each constituent have average values related to different compositions of slag.

Nevertheless, the complex information in this table makes it possible to assess the overall quality and quantity of the waste products.

CANADIAN SLAG

The quantities shown below relate to 1 tonne of finished product and are based on the value in the preceding table.

Waste product 1 - Insoluble substances

107 kg

(SiO₂, TiO₂, Al₂O₃, MgO, Cr₂O₃, P₂O₅, MnO, V₂O₅, CaO, Si, Ni, Zn, Cu, Cd, Be, Sb, Hg)

+ 107 kg

H₂O (assuming H₂O = 50% of total weight)

214 kg

Waste product 2 - Copperes

None

Waste product 3 - Strong acid

630 kg

various sulphates, including 303 kg of FeSO₄

+ 34 kg

TiO₂ in suspension

+ 33 kg

TiO₂ in solution

+ 1,440 kg

H₂SO₄ (exp. as 100%) concentration

+ 5,063 kg

H₂O

7,200 kg

Waste product 4 - Weak acid

339 kg

various sulphates, including 163 kg of FeSO₄

+ 28 kg

TiO₂ in suspension

+ 19 kg

TiO₂ in solution

+ 778 kg

H₂SO₄ (exp. as 100%) concentration 10%

+ 6,624 kg

H₂O

7,780 kg

WASTE PRODUCTS CORRESPONDING TO ORE D.

ENRICHED MINERAL (Hypothetical)

(Similar to Canadian slag)

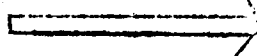
ORIGINAL ORE		
ENRICHED ORE		
	%	kg
TiO ₂	88,00	1130,000
FeO	5,00	64,204
Fe2O3	0,50	6,420
SiO2	1,65	21,187
ZrO2	-	-
Al2O3	2,00	25,681
P2O5	0,01	0,128
MnO	0,08	1,027
MgO	2,00	25,681
Cr2O3	0,10	1,284
V2O5	0,20	2,568
CaO	0,40	5,136
Na2O	-	-
K2O	-	-
S	0,02	0,256
NiO	0,03	0,385
Zn	-	-
Cu	0,01	0,128
Cd	-	-
Pb, Be	-	-
Sb, Hg	-	-

Yield 88.5%



PRODUCT
TiO ₂ : 1 tonne

Waste products



FATAL WASTE PRODUCTS	
Expressed as quantities of metal (kg)	
Ti	78,000
Fe	52,133
Si	9,746
Zr	-
Al	6,779
P	0,026
Mn	0,795
Mg	15,408
Cr	0,422
V	0,680
Ca	3,538
Na	-
S	0,256
Ni	1,068
Zn	-
Cu	0,101

Corresponding weight of ore: 1,284 kg.

ENRICHED ORE

The quantities shown below relate to 1 tonne of finished product and are based on the values in the preceding table.

Waste product 1 - Insoluble substances

	57 kg	(SiO ₂ , TiO ₂ , Al ₂ O ₃ , MgO, Cr ₂ O ₃ , P ₂ O ₅ , MnO, V ₂ O ₅ , CaO, Si, Ni, Zn, Cu, Cd, Be, Sb, Hg)
+	57 kg	H ₂ O (assuming H ₂ O = 50% of total weight)
	<hr/>	
	114 kg	

Waste product 2 - Copperas

None

Waste product 3 - Strong acid

	185 kg	various sulphates, including 98 kg of FeSO ₄
+	34 kg	TiO ₂ in suspension
+	31 kg	TiO ₂ in solution
+	1,395 kg	H ₂ SO ₄ (exp. as 100%) concentration 20%
+	5,330 kg	H ₂ O
	<hr/>	
	6,975 kg	

Waste product 4 - Weak acid

	100 kg	various sulphates, including 53 kg of FeSO ₄
+	28 kg	TiO ₂ in suspension
+	17 kg	TiO ₂ in solution
+	750 kg	H ₂ SO ₄ (exp. as 100%) concentration 10%
+	6,605 kg	H ₂ O
	<hr/>	
	7,500 kg	

2) Disposal or treatment of the waste products inherent in the process

1 - Definition

"Elimination or treatment of waste products inherent in the process" is understood to mean any intervention which leads to a change in their characteristics, which can range from mere dilution in order to reduce the concentration to very elaborate operations radically changing the nature of the waste.

2 - List of the main methods of elimination and treatment that can be envisaged for "waste products inherent in the process"

DISCHARGE INTO THE SEA (1)* This can be done direct from the coast or by scattering over the sea. This method is widely used for soluble waste products (copperas and acid solutions).

Injection into underground strata This requires special geological conditions. Its use in the United States (DuPont) has given rise to strong criticism. The "injected" effluents must not contain suspensions which might clog the well.

STORAGE ON LAND (2) This is used for insoluble waste products. Storage on land of soluble waste products ("copperas") raises more problems owing to their solubility and their large quantities. The company THANN & MULHOUSE, in Thann (France), stores on land insoluble products, "copperas" and the neutralisation products of its acid liquors (output 20,000 tonnes per annum of TiO_2).

NEUTRALISATION (3) This method, which results in a very large volume of neutralisation product, is very little used. Its cost is high. At present, in Europe, only THANN & MULHOUSE uses this method for its acid liquors (at Thann). In the United States, "SCM" neutralises the dilute acid fraction. The neutralised products are rediluted and discarded.

(*) Only the numbered methods can be envisaged, a priori, in the European context.

Production of gypsum: Production of gypsum from the neutralisation of the acid liquors requires a special local context. In the United States the American Cyanamid company is building a factory for producing building components of gypsum. It should be noted that in this case there are no local gypsum resources; moreover, the local types of buildings are well suited to the use of such a material.

LURGI COPPERAS-
DRYING PROCESS (4)

This method enables "copperas" compounds to be dehydrated by changing them into iron sulphate monohydrate, which can be roasted in a fluidised-bed furnace (there is an existing unit at Spinetta, Italy, and one being built at Celje, Yugoslavia).

Fluidised-bed drying
of copperas compounds

Process employed by BAYER to enable iron sulphate to be roasted in rotary furnaces.

LURGI FLUIDISED-BED
ROASTING PROCESS (5)

The LURGI roasting process makes it possible to treat iron sulphate monohydrate ("copperas" after dehydration) or concentrated acids (70%) containing salts in solution. One obtains, from the solid or liquid substance fed in, on the one hand SO_2 which can be directly used in an H_2SO_4 synthesising unit and, on the other hand, the metal oxides corresponding to the salts in solution. There is no experience yet of working with liquid feed.

ROASTING IN A ROTARY
FURNACE (6)

This technique, which is an old one, makes it possible to treat "copperas" compounds after dehydration or salts precipitated during concentration of acid liquors. Actually the need to use sulphur or pyrites to bring about combustion leads to the production of quantities of H_2SO_4 greatly in excess of the requirements of a TiO_2 unit. This method has been employed marginally by Bayer - Titangesellschaft - Pigment Chemie in Germany and by British Titan Products at Grimsby (Great Britain).

"NEW JERSEY ZINC"
PROCESS (7)

This process can be used for treating acid liquors. After treatment pure sulphuric acid is obtained, together with iron sulphate monohydrate mixed with the other elements present in the solution. At present the only plant based on this process is a small pilot in the United States.

LURGI ACID-
CONCENTRATION
PROCESS (8)

This process "treats" acid liquors by bringing them up to a concentration of 70%. The acid is not evaporated, and the 70% acid still contains all the salts in solution. No actual unit based on this principle.

BAYER ACID-
CONCENTRATION
PROCESS (9)

Bayer uses a process of concentration by submerged flame. This process has proved very unsatisfactory.

BAYER- BERTRAMS
ACID-CONCENTRATION
PROCESS (10)

This process for concentration of acid liquors uses a film evaporator. There is still little information about the possibilities of using it in the TiO_2 industry.

Production of
superphosphate

Superphosphate is a fertiliser the use of which in Europe has considerably declined. It is obtained by attacking natural tricalcium phosphate with sulphuric acid. At present only one state-owned company in Poland uses this process, which requires prior concentration of the acid liquors up to 65%

Ammonium sulphate
production

This process enables ammonium sulphate to be produced from acid liquors. Ishihara Sangyo Kaisha holds the rights to a process making possible the optimum treatment of acid liquors by this method. Ammonium sulphate is no longer used in Europe, and this method is thus of little interest at present, at least in Europe.

I.F.P. PROCESS (11)

This process enables dissolved sulphates to be treated. It thus makes it possible to treat either acid liquors alone or acid liquors in which the "copperas" compounds have been previously redissolved. The products obtained are sulphur and hydroxides and sulphides of the metals in solution.

To these processes should be added those of the BUTTNER and SAINT GOBAIN companies, described as "new techniques" in the field of acid concentration.

Note: In the Netherlands there is a system of taxation of effluents.

Its amount at present represents about 3.5% of the cost of TiO_2 .

I It is said that this tax is to be doubled every year.

SECTION 3 - Treatment units and final waste products

A. ATIS

In Section 2 a list has been given of the processes which could be used for the treatment of waste products inherent in the production process.

In this section an attempt will be made, by combining the various proposed processes, to establish complete treatment units. There are obviously very many possibilities, and only the most characteristic ones have been considered.

Furthermore, depending on the degree of treatment which it is desired to achieve, the units proposed can either be adopted as a whole or some of their constituent parts replaced or even omitted.

The capital investments and operating costs involved for each of these units will be stated. The capital investment figures are based only on design data available at present, and the operating costs have been calculated on the basis of values recorded at a fixed date (end of 1973) and are now being updated in the light of the present economic situation. The characteristics and volumes of the final effluents will also be given.

These solutions will be considered for the different types of raw materials.

B. BASIC DATA

Below and on the following page, the weights of effluents to be treated corresponding to an output of TiO₂ of 100 tonnes per day are given for the four types of raw materials.

	Norwegian ilmenite	Australian ilmenite	Canadian slag	Enriched ore
1) <u>INSOLUBLE SUBSTANCES</u>				
<u>Total weight</u>	16 t/d	3.8 t/d	21 t/d	11 t/d
Volume if d = 2*	32 m ³ /d	7.6 m ³ /d	42 m ³ /d	22 m ³ /d
"Dry" weight**	8 t/d	1.9 t/d	10.5 t/d	5.5 t/d
2) <u>COPPERAS</u>	t/d	t/d	t/d	t/d
<u>Total weight</u>	385	202		
FeSO ₄ , 1.1/2 H ₂ O	189	111	does not exist	does not exist
MgSO ₄	20.4	1.1		
exp. in H ₂ SO ₄	122	62		
exp. in Fe ₂ O ₃	169	99		

* d: density of the insoluble substances as a whole
(d = 2 is a hypothetical value)

** represents the weight of the insoluble substances if
water is excluded from them.

	Norwegian ilmenite	Australian ilmenite	Canadian slag	Enriched ore
3) <u>ACID LIQUOR</u> (hypothetical concentration 20%)	t/d	t/d	t/d	t/d
<u>Total weight</u>	741	625	720	697
H ₂ O	512	429	506	533
Free H ₂ SO ₄	148	125	144	140
FeSO ₄	58	58	30	10
Various sulphates	14	5	32	9
H ₂ SO ₄ (free + combined)	195	165	184	152
Exp. in Fe ₂ O ₃	61	61	31	11
Exp. in sulphur	64	54	60	50
4) <u>DILUTE ACID</u> (hypothetical concentration 10%)	t/d	t/d	t/d	t/d
<u>Total weight</u>	800	672	778	750
Free H ₂ SO ₄	80	67	78	75
H ₂ O	675	566	652	660
FeSO ₄	31	31	16	5
Various sulphates	8	3	18	5
H ₂ SO ₄ (free + combined)	106	89	99	82
Exp. in Fe ₂ O ₃	33	33	17	5
Exp. in sulphur	35	29	32	27

C. COST ASSESSMENT

a) Capital investment

For each treatment unit the total capital investment is determined from the capital investments for each constituent part. These are for the period end 1973 - beginning 1974 and must therefore adjusted in the light of the present economic situation.

Allowance has also been made for the price of recovering the sulphur or sulphuric acid as the case may be, excluding all other products, particularly FeO.

b) Energy consumption

For each treatment the energy consumptions for the different types of raw materials have been established.

For the price of fuel oil, an average price of 50 U.A. per tonne has been assumed. It should be noted, however, that the processes treating gases containing SO₂ are not interfered with by the use of very sulphurous fuel oil such as "vacuum residues". These two processes are the roasting process (LURGI) and the I.F.P. process.

The value of the "vacuum residues", always less than that of fuel oil, will depend on the particular situations of each petroleum group, the location of the refinery and its distance from the consuming factory.

Depending on the situation, the "vacuum residue" may cost the consumer between 80% and (exceptionally) 60% of the price of ordinary heavy fuel oil. In the present case the possible use of "distillation" residues" costing 40 U.A. per tonne has been assumed.

Note: It will be recalled that, for roasting, sulphur can be used as a fuel, which in some cases makes it possible to reduce consumption of fuel oil. This possibility depends greatly on local conditions; it should merely be borne in mind that the fuel-oil consumptions shown for roasting are high values.

c) By-products

In practice we shall consider only three categories of by-products:

- sulphur
- sulphuric acid
- ferric oxide (part) or ferric hydroxide (part).

A sulphur "credit" will be included in cases where the sulphates and/or sulphuric acid are decomposed in the form of SO_2 or elementary sulphur.

A "sulphuric acid" credit will be included whenever recycling of this acid can be done directly and therefore does not entail additional capital expenditure.

The savings are based on the following values:

sulphur	: 52 U.A./t
sulphuric acid:	: 29 U.A./t

Note: As the price of sulphur varies greatly, a treatment cost corresponding to a sulphur price of 30 U.A./t and thus to a sulphuric acid price of 22 U.A./t has also been given.

With regard to iron in oxide or hydroxide form, only iron obtained from copperas will be regarded as a by-product which may possibly be reusable, but its value will be assumed to be zero.

D. RECAPITULATION

Treatment units which can be envisaged
for the titanium dioxide industry

Constituent processes	Ref.	Capital investment (U.A./t. per annum of TiO ₂)	Waste products after treatment
(Dehydration) - Lurgi	I	Ilm 263	(Iron oxide) ^o
Roasting - Lurgi			Iron oxides + various
Concentration - Lurgi			CaSO ₄ , Fe(OH) ₂
Neutralisation		Slag 195	Water
(Dehydration) - Lurgi	II	Ilm 273	(Iron oxide) ^o
Roasting - Lurgi			(Iron oxides + various
Concentration - N.J.Z		Slag 195	CaSO ₄ , Fe(OH) ₂
Neutralisation			Water
(Dehydration) - Lurgi		Ilm. 338	(Iron oxide) ^o
(Roasting) - Lurgi	III		Fe(OH) ₂ + various sulphates
IFP process		Slag 245 245	CaSO ₄ , Fe(OH) ₂
Neutralisation			Water
IFP process	IV	Ilm 339	(Iron hydroxide) ^o
			Fe(OH) ₂ + various sulphates
		Slag 254	Water
(Dehydration) - Lurgi			(Iron oxide) ^o
(Roasting) - Lurgi	V	Ilm 351	Fe(OH) ₂ + various sulphates
IFP process		Slag 259	Water
(Dehydration) - Lurgi			(Iron oxide) ^o
Roasting - Lurgi	VI	Ilm 312	Iron oxide + various
Concentration - N.J.Z.		Slag 233	Water

Note 1: The substances in brackets disappear if slag is used

Note 2: The waste products marked (o) may be reusable. They have been assigned zero value in the economic calculations.

Cost of the main methods of treatment which can be envisaged for the titanium dioxide industry
(Sulphate process)

Treatment	Raw Material	Hypotheses			
		Fuel oil: 50 UA/t Sulphur 52 UA/t H ₂ SO ₄ 29 UA/t	Fuel oil + dist. res. 40 UA/t Sulphur 52 UA/t H ₂ SO ₄ 29 UA/t	Fuel oil 50 UA/t + dist. res. 45 UA/t Sulphur 30 UA/t H ₂ SO ₄ 22 UA/t	
		UA/t of TiO ₂	UA/t of TiO ₂	UA/t of TiO ₂	
I	Ilm.	97.3	90.8	113.6	
	Slag	77	72.8	86	
II	Ilm.	77.4	74.7	95.2	
	Slag	53.8	53.4	64.7	
III	Ilm.	134	124.2	145.7	
	Slag	105.6	97.6	110.8	
IV	Ilm.	126	100	130	
	Slag	94.3	82.9	112.2	
V	Ilm.	122	108	138.4	
	Slag	89.3	77.9	112.2	
VI	Ilm.	95.4	92.1	108	
	Slag	52.1	50.9	66.4	

Note - This is an estimate made at the end of 1973/beginning of 1974.

A more up-to-date estimate is being prepared.

Special characteristics of the main methods of treatment which can be envisaged for the titanium dioxide industry (sulphate process)

- TREATMENT I - low cost
- concentration process not yet industrially proved
- neutralisation waste products rather inconvenient to store
- TREATMENT II - Same comments as for Treatment I
- TREATMENT III - Juxtaposition of several fairly reliable processes
- high cost
- neutralisation waste products rather inconvenient to store
- TREATMENT IV - only one process used (IFP)
- relatively high cost
- final waste products a priori less convenient than oxides
- TREATMENT V - complex of quite reliable processes
- rather high cost
- final waste products a priori less convenient than oxides
- TREATMENT VI - "Concentration section" not industrially proven
- cost sensitive to the concentration of the weak acid
- final waste products fairly convenient to store and/or possibility of reuse.

SECTION III. CHLORINE PROCESS

Waste products inherent in the process

1. General

a) Introduction

As already mentioned, the only purpose of the calculations made in this section is to give orders of magnitude for the quantities of waste products to be considered.

Admittedly, in view of the fact that the chlorine process is little used in Europe and that the information about it is generally confidential, it has only been possible to make rather rough hypotheses for this process.

However, although these hypotheses may prove inaccurate, the quantitative approach to the total effluents remains valid.

b) Hypotheses

We have assumed that:

- the overall operating yield is 98% in relation to the TiO_2 involved, excluding the finishing (surface treatment) stage. This type of treatment has already been seen for the sulphate process. With regard to effluents, it leads only to dilute salt solutions and a small quantity of TiO_2 in suspension.
- The zirconium oxide present in the ore is not attacked.
- All the other metals and metalloids are chlorinated.
- 1% of the raw ore is lost in the "blow-offs" of the fluidised bed and by entrainment in the process gases.
- 0.5% of the titanium dioxide is lost in the form of $TiCl_4$.
- 2% of the chlorine necessary for the chlorination of the titanium dioxide is lost through combination with hydrogen from the reduction coke and the ore.

- For the $TiCl_4$ "oxidation" section

- . 0.5% of the TiO_2 involved is lost in solid form
- . with regard to the effluents resulting from possible liquefaction of the chlorine, these are very traditional in nature and have been disregarded in the present technical report.

c) Distribution of the different waste products

It has already been seen in the description of the chlorine process that the four major sources of waste products are:

- . waste product 1 - "blow-off" from the fluidised bed
- . waste product 2 - "residues" of the distillation of $TiCl_4$
- . waste product 3 - "venting" from the distillation of the $TiCl_4$
- . waste product 4 - waste from the oxidation stage.

The melting and evaporation temperatures of the chlorides of the different metals make it possible to some extent to predict the distribution of these chlorides in the waste products. Furthermore, certain hypotheses have been made for the distribution of the losses of ore, $TiCl_4$ and chlorine.

. Waste product 1

The whole of the ZrO_2 , $MnCl_2$, $MgCl_2$, $CaCl_2$, $NaCl$.
Half of the ore losses.

. Waste product 2

The whole of the $FeCl_3$, $AlCl_3$, $CrCl_2$, $NbCl_5$
The vanadium is present in the form of $VOCl_2$
Half of the ore losses.

. Waste product 3

The whole of the $SiCl_4$, PCl_3 ($POCl_3$)
The whole of the losses of HCl and $TiCl_4$

2 - A. WASTE PRODUCTS CORRESPONDING TO NATURAL RUTILE ORE

ORIGINAL ORE			PRODUCT			
NATURAL RUTILE			TiO ₂ : 1 tonne			
	%	kg				
TiO ₂	96.50	1020.400	Yield 98% FATAL WASTE PRODUCTS expressed as quantities of metal (kg)			
FeO	-	-				
Fe ₂ O ₃	0.35	3.696				
SiO ₂	0.35	3.696				
ZrO ₂	0.65	6.866				
Al ₂ O ₃	0.45	4.752				
P ₂ O ₅	0.05	0.527				
MnO	0.02	0.211				
MgO	0.06	0.633				
Cr ₂ O ₃	0.30	3.169			Waste Products	
V ₂ O ₅	0.66	6.971			Ti	12.240
CaO	0.01	0.105			Fe	1.219
Na ₂ O	-	-			Si	1.700
K ₂ O	-	-			Zr	5.032
S	-	-	Al	1.254		
H ₂ O	-	-	P	0.106		
Co	-	-	Mn	0.163		
C	-	-	Mg	0.380		
NbO ₂	0.30	3.169	Cr	1.042		
H	0.20	2.113	V	1.874		
			Ca	0.072		
			Na	-		
			S	-		
			Ni	-		
			Zn	-		
			Cu	-		
			Nb	2.352		
			H	2.111		

Total 1056 kg

Typical composition

Distribution of effluents:

- waste product 1: 14 kg/t of TiO₂ (ZrO₂ + various chlorides + ore)
- waste product 2: 30 kg/t of TiO₂ (+ various chlorides)
- waste product 3: 59 kg/t of TiO₂ (+ various chlorides)

2 - B. WASTE PRODUCTS CORRESPONDING TO SYNTHETIC RUTILE ORE
(Benelite type)

ORIGINAL ORE			Yield 98%	PRODUCT	
SYNTHETIC RUTILE				TiO ₂ : 1 tonne	
	%	kg			
TiO ₂	95	1020.40			
FeO	1.8	18.96			
Fe ₂ O ₃	2.0	21.60			
Various	1.2	13.09			
				FATAL WASTE PRODUCTS	
				Expressed as quantities of metal (kg)	
				Ti 12.240	
				Fe 22.665	
				Various (13.09)	

Waste products

Corresponding weight of ore: 1074 kg

Distribution of effluents:

Waste product 1: 14 kg/t of TiO₂

Waste product 2: 90 kg/t of TiO₂

Waste product 3: 59 kg/t of TiO₂

2 - C. WASTE PRODUCTS CORRESPONDING TO AUSTRALIAN ILMENITE ORE

ORIGINAL ORE			Yield 98%	PRODUCT	
AUSTRALIAN ILMENITE				TiO ₂ : 1 tonne	
	%	kg		FATAL WASTE PRODUCTS	
TiO ₂	55.4	1020.20		expressed in quantities of metal (kg)	
FeO	23.8	438.361		Ti	12.240
Fe ₂ O ₃	16.9	311.350		Fe	449.513
SoO ₂	0.15	2.763		Si	1.264
ZrO ₂	-	-		Zr	-
Al ₂ O ₃	0.94	17.337		Al	4.569
P ₂ O ₅	0.08	1.489		P	0.297
MnO	0.72	13.274		Mn	10.267
MgO	0.27	4.966		Mg	2.979
Cr ₂ O ₃	0.14	2.753		Cr	0.848
V ₂ O ₅	0.17	3.160		V	0.830
CaO	0.02	0.361		Ca	0.252
Na ₂ O	-	-		S	0.180
K ₂ O	-	-	Waste products	Ni	-
S	0.01	0.180		Zn	-
Ni	-	-		Cu	-
Zn	-	-		Ce	-
Cu	-	-		Pb, Be	-
Cd	-	-			
Pb, Be	-	-			
Sb, Hg	-	-			

Corresponding weight of ore 1,842 kg

N.B. The total of the column does not correspond to 2,040 kg, as the weights of each constituent have average values related to different compositions of ilmenite.

Distribution of effluents:

Waste product 1: 44 kg/t of TiO₂ (ZrO + various chlorides + ore)

Waste product 2: 1,339 kg/t of TiO₂ (various chlorides including 1,304 kg of FeCl₃)

Waste product 3: 76 kg/t of TiO₂ (various chlorides)

3 - Treatments

A. Effluents considered

As stated earlier, the chlorine process is little used in Europe. In all cases the installed capacity is small.

Moreover, these units at present use natural rutile, that is, an ore very rich in TiO_2 (about 96%), which therefore gives rise to only fairly minor quantities of effluents.

These two factors mean that the problem of the effluents of the chlorine process does not really arise in Europe.

Nevertheless, the main treatments which can be envisaged in this case will be examined, firstly because even though the chlorine process is at present little used in Europe, it is nevertheless under certain conditions a valid alternative to the sulphate process, and secondly because the possibilities of development of synthetic rutile or the possibility of using a poorer ore may lead to a change in the present positions.

It may be noted that in the United States, where the chlorine process is very widespread and where DuPont is said to use a relatively poor ore in one of its factories, the problem of the effluents of this process has arisen.

DuPont, which is the company most involved in this direction, has not yet succeeded, despite major research efforts and strong economic incentives, in perfecting the regeneration of the chlorine by oxidation of the by-product chlorides.

After having envisaged discharge into underground strata, it would appear that DuPont has decided to opt for discharge at sea.

The following will not be considered in this chapter:

- the effluents of the "regeneration" unit for the chlorine to be recycled, as these are traditional and not specific to this industry;
- the effluents corresponding to the finishing operations (surface treatment); these are not peculiar to this process.

We shall deal here with the treatment of the chlorides which are formed simultaneously with the titanium tetrachloride and which are separated in the further course of the process.

Three sources of waste products for this type of effluent and for this process have been listed. These effluents are identified as "waste product 1, 2 and 3".

B Main processes

The considerations regarding the discharge of effluents into underground strata or at sea will not be repeated here. These eventualities have already been examined within the framework of the "sulphate" process (page 21).

It may be noted, however, that these are the only two methods which have been adopted in practice in the United States; underground discharge has incidentally been strongly criticised.

The only two processes which seem to represent a possible treatment for this type of effluent are ones which enable the metallic chlorides to be broken down into oxides, the chlorine then being combined to form HCl.

Actually these two processes are fairly similar in principle, the main difference being their type of feed:

- chlorides in solution in one case,
- solid chlorides in the other case.

The companies holding the rights to these processes are WOODALL DUCKHAM and LURGI respectively.

It should also be noted that the company "CHLORINE TECHNOLOGY Ltd", which is engaged in the recuperation of ilmenite, is said to hold the rights to a process for the oxidation of the chlorides, but this is not yet regarded as very satisfactory. There is no doubt, however, that companies other than those enumerated above are likely to develop processes which would be based on similar principles.

It may also be mentioned that in the two cases referred to above it is a question of adapting existing, proven processes whose application has not yet, however, been tested in this particular field.

PART 2

ECOLOGICAL ASPECTS

GENERAL

Examination of the results already obtained

Examination of international scientific documentation on the effects of discharging the residues from the production of titanium dioxide into the sea leads us to regard these waste products as potentially or actually harmful to the marine aquatic medium.

The degree of harmfulness of the residues may vary depending on their composition, the method of discharge and the characteristics of the receiving medium. The adverse effects on the environment are due mainly to the acidity, to the presence of ferrous sulphate and probably to the other metals (heavy metals) which are also present.

Depending on the cases, the adverse effects on the environment can take the following forms:

- 1) reduction of the oxygenation and pH of the water and increase of the concentration of iron and other heavy metals. The duration and extent of these effects depend on the physico-chemical characteristics of the waste products, and especially their concentration;
- 2) a) temporary depletion of the zooplanktonic biomass and production of effects leading to a deterioration in the morphological structure of its component parts;
b) repulsion and removal of certain species of fish;
c) reduction of the biomass and of the production and diversity of species of the benthic and/or nectobenthic biocenoses in the discharge area. In more serious cases all animal life may disappear.

- 3) deterioration in the colour, transparency and turbidity of the water and temporary reduction of photosynthesis, phytoplankton and primary production, especially in cases where the waste is discharged on the surface. Covering of the sea bed with ferric oxides and oxides of other metals where the waste is discharged in estuaries and places where the water is shallow;
- 4) on the other hand, there have been no reports of dangers of toxicity for human beings due to effects produced by the consumption of species from the places where the waste has been discharged.

The degree to which the above-mentioned phenomena occur varies depending on the different methods of discharge. There is not, however, a single case in the scientific literature published or mentioned by the various experts of the Member States in which one or more of these phenomena have not been recorded.

All this leads to the conclusion that discharge into the sea of waste from the production of TiO_2 must be controlled and even suspended within a certain period in order to prevent damage to the marine environment, now and in the future.

As an illustration of the effect of the disposal of effluents of the TiO_2 industry, the results of the "White Book" published by France in connection with the discharging of the Montedison company's waste products into the Mediterranean Sea are reproduced on the following pages.

CHAPTER V - ESTIMATE OF THE PHYSICO-CHEMICAL CHANGES DUE
TO THE DISCHARGES

The following analysis deals mainly with the physico-chemical changes (in pH, saturation indices, change in natural concentration, etc.) which may be caused by discharges such as those made by the Montedison company.

1) Three major factors must be considered

As has been stated earlier, the waste products are characterised by:

- high acidity due to the presence of large quantities of free sulphuric acid in the effluents: we must therefore assess the reactions of sea water when faced with the introduction of 330 tonnes of pure sulphuric acid per day.
- a high content of divalent iron Fe^{++} : the commonest form of iron in the sea is trivalent iron Fe^{+++} ; the mechanisms of this oxidation in sea water must therefore be considered.
- a by no means negligible content of heavy metals such as titanium, chromium, vanadium, cadmium, etc.

2) Reaction of sulphuric acid

Sea water is a medium with a very strong buffer capacity with regard to acids and bases. This buffer capacity is bound up with the balance of the carbon dioxide gas, bicarbonate-carbonate system. It takes 3 milli-equivalents of strong acid per litre to transform the carbonates and bicarbonates into carbon dioxide gas and reach a pH of about 6.

On this basis it can be calculated that it takes 12 m^3 of sea water to "buffer" one litre of pure sulphuric acid (pH brought back to a value of 6 or above).

It is assumed (American papers) that 15 m^3 of sea water completely neutralise 1 litre of pure sulphuric acid.

On the basis of the above values (330 tonnes of H_2SO_4 discharged per day) a neutralisation volume of

$$\frac{15 \times 330,000}{1.8} = 2,800,000 \text{ m}^3$$

is obtained.

In order to establish an order of magnitude, the area within which a daily discharge is neutralised may be estimated at about 20 hectares if it is assumed that the discharged waste diffuses slowly in a vertical direction whatever the depth at which it is discharged and that it only affects a layer of water about 10 m thick (cf. the conclusions of the C.N.E.X.O. report on horizontal and vertical transmissions in the area).

3) The oxidation of divalent iron into trivalent iron

While seawater has a buffer capacity as regards acid-base equilibria, the position is different as regards oxidation-reduction couples. That is why it must be assumed that high oxygen demands can only be satisfied by utilisation of the oxygen dissolved in the sea water.

If we assume that it takes one molecule of oxygen to oxidise 4 Fe^{2+} ions into 4 Fe^{3+} ions, we arrive at the following calculation:

140 tonnes of divalent iron discharged per day
need in order to be oxidised:

$$\frac{140}{56} \times \frac{32}{54} = 20 \text{ tonnes of oxygen}$$

It may be mentioned in this connection that this represents approximately the oxygen demand of the sewage of a town with:

$$\frac{20 \cdot 10^6}{60} = 350,000 \text{ inhabitants (1)}$$

(1) This is an important point and enables us to relate these discharges to those of the coastal towns of the Côte d'Azur and the Gulf of Genoa.

The available data concerning this area indicate a quantity of dissolved oxygen of 8 mg/litre, or 8 g/m³. The volume of water required for complete oxidation of the waste is therefore (assuming that the oxidation takes place near the surface):

$$\frac{20 \cdot 10^6}{8} = 2,500,000 \text{ m}^3$$

(It will be noted that there is a fair degree of similarity between this value and the volume required to "buffer" the effluent, although it is necessary to emphasise the approximate nature of the above two calculations, the sole purpose of which is to provide orders of magnitude.)

- It would however be misleading to picture an actual volume of $3 \cdot 10^6 \text{ m}^3$ affected by the sulphuric acid: in fact, only programmes of measurements carried out on the spot can permit a more accurate determination of the volume involved, which is probably smaller owing to the turbulences which appear at the surface of the streams of waste products and which have the effect of spreading out the period during which the dilution phenomenon takes place.
- Similarly, the oxidation of the divalent iron into trivalent iron is probably a long-term phenomenon: the experimental results obtained both at the place of the waste discharges and in the North Sea or in New York Bay represent a slow oxidation, which never reduces the oxygen saturation index of the area by more than 30%.

It is therefore logical to assume that the discharges of waste products cause the formation of a mass of water with a small oxygen deficit, but much larger in volume than has been envisaged.

4) Role and behaviour of the heavy elements such as chromium, vanadium, cadmium and titanium

It has been thought necessary to devote a paragraph to recalling certain overall data concerning the presence and possible role of such elements, which have recently led to the adoption of some contradictory attitudes.

1 - It must be recalled in the first place that all these elements are naturally present in sea water, as is shown by the figures taken from Riley and Skirrow (1965) and Ivanoff (1972) in the following comparative table.

Elements	Weight present in 1 kg of rock (average) in mg	Concentration in sea water in mg/l	Weight present in 1 kg of pelagic sediment in mg	Residence time in the sea in years (1)
Si	275,000	3	199,000	8 10 ³
Al	83,000	0,01	65,000	100
Fe	52,000	0.01	41,000	140
Hg	22,000	1,300	17,000	4.5 10 ⁷
Ti	6,300	0.001	3,500	160
Mn	930	0.002	3,200	1,400
V	120	0.002	330	10 4
Cr	65	0.00005	80	350
Cd	0.5	0.0001	?	5 10 ⁵
Pb	15	0.00003	160	2 10 ³

(1) The "residence time" of an element in the sea is equal to the average time for which this element remains in the sea water before disappearing by sedimentation or biological absorption. A short residence time for an element which is assumed to be toxic (a favourable factor from the overall point of view) is therefore not a reassuring criterion from the point of view of the consumer of the products of the sea, insofar as this rapid elimination is partly achieved thanks to concentration phenomena in the biological chains.

It will thus be seen that the chemical composition of rocks is fairly close to that of sediments. On the other hand, the relative composition of sea water is entirely different from that of the earth's crust, a fact which implies the existence in the sea of processes which limit the concentration of certain elements although they are continually provided by rivers, run-off water and wind-borne matter.

The intensity of the action produced by these mechanisms on the various elements is well represented by the "residence times", which can range from around 100 years for aluminium, iron and titanium to several tens of millions of years for certain alkaline and alkaline-earth substances.

The processes of regulation ultimately tend to eliminate certain elements from sea water by incorporating them in the sediments. They are physico-chemical (formation of complexes, co-precipitation, absorption and ion exchanges on the particles or at the sediment levels) and biological in nature. (Many marine organisms selectively concentrate certain elements. During mineralisation of organic matter, a portion sediments and represents a loss for the sea water).

- 2 - With regard more specifically to titanium, it will be seen that this element is one of the main constituents of the earth's crust, representing about 0.5% by weight. It is almost equally abundant in sediments. It is present in very low concentration in sea water; its residence time has been estimated at 160 years. By its characteristics it is closely akin to the three most abundant constituents of the earth's crust: silicon, aluminium and iron. Titanium is regarded as physiologically inert.

The trace elements, hexavalent chromium (1) and above all cadmium are well-known for their toxicity. Vanadium would also appear to be toxic,

(1) Chromium is harmful in its hexavalent form, but in the sea it is quickly changed back to its less dangerous trivalent form. The chromium contained in the waste from the manufacture of titanium dioxide is already in the form of a trivalent oxide.

but there is as yet relatively little literature on this point.

- 3 - In order to give a clearer idea of the actual scale of the trace elements discharged with the waste products of the Montedison company, it was therefore thought worthwhile, on the basis of the foregoing information, to prepare the following table:

Elements	Weight present in 3000 t of rock in kg	Weight present in the 3000 t of waste products from the manufacture of 150 t of TiO_2 /day (kg)
Fe	156,000	145,000
Ti	18,900	7,800
Mn	2,790	1,750
V	360	710
Pb	45	30
Cd	1.5	30
Cr	195	100

This table brings out the similarity which exists between the quantities of heavy metals present in the waste and in the same weight of rocks; but this similarity is relative, because it must be pointed out that the effluents contain vanadium and cadmium in larger proportions than the rocks.

Such figures do not warrant the drawing of any conclusion regarding the direct or induced toxicity attributable to heavy metals in the waste products: part of these is dissolved in the liquid effluent, which is not true of those which are contained in rocks.

When the effluents are diluted, a large proportion of the metals precipitate in mineral form and produce a sediment on the sea bed. The phenomena of indirect toxicity are bound up with the two portions (dissolved and precipitated) of the metal salts in the waste.

The comparison made is therefore only of overall value, being quantitatively valid in relation to the geochemistry of the whole of the Ligurian basin. It should furthermore be recalled that this area naturally receives quite substantial quantities of heavy metals naturally entrained by rivers as the soil is washed and eroded.

CHAPTER VI - STUDY OF THE BIOLOGICAL EFFECTS OF
EFFLUENT DISCHARGES

The different aspects of the problem

The study of the possible effect of the discharging of industrial effluents into the sea is an extremely complex matter. For this effect has two different aspects:

- a short-term effect by direct or "acute" poisoning, which can even lead to the killing of living beings in the immediate vicinity of the discharge area. In the specific case of the waste products of Montecatini Edison, this effect will be mainly due to their high sulphuric acid and iron content.
- an indirect long-term toxic effect by the accumulation of certain elements in food chains. This phenomenon does not necessarily lead to major disorders in marine life itself. Problems may arise, however, at the level of human consumption of fish or molluscs which have accumulated high contents of undesirable elements in the geographical area of the waste discharges.

In the case of the discharges of the Montedison company, their indirect toxicity may be due to their content of heavy metals: titanium, vanadium, cadmium and chromium.

For the purpose of studying the biological influence of the waste products it is therefore necessary to distinguish between these two main directions of investigation. They can be covered:

- by biological observations "on the spot"
- by laboratory experiments.

The studies of direct or indirect toxicity carried out in laboratories are all based on observations of the behaviour of marine plants or animals placed for fairly long periods in variable concentrations of the effluent under test.

It is important to emphasise this "time" aspect at the outset, since in the natural environment a certain number of the species tested will tend to flee from the most active zone of the waste matter and will finally only be exposed for relatively short periods to the weakest dilutions of effluents.

Many investigations have been made into the toxicity of the waste products of the Montedison company or of similar waste.

The results at present known will be given, in the light of the foregoing, under the following main heads:

- analysis of the short-term effects
- analysis of the possible long-term effects.

SECTION I - THE SHORT-TERM EFFECTS

1) Data on the behaviour of the marine flora and fauna in the vicinity of the discharges

a) Behaviour of macroscopic animals

It is important to emphasise this point, which may have led to misunderstandings in recent months: it has never been possible to observe in the discharge zone any abnormal mortality of macroscopic animals such as fish, molluscs or marine mammals.

Furthermore, none of the various reports of the five missions carried out on the spot by French technicians mentions the presence of bodies of animals on the surface of the water.

With regard to the stranding of sperm-whales and cetaceans which has taken place fairly recently in the Mediterranean, the conclusions of the report of the Institut Scientifique et Technique des Pêches Maritimes are as follows :

"With regard to the strandings of cetaceans in Corsica, we have been able to analyse the muscle and fat of a sperm-whale stranded near Bonifaccio. It appears that the mercury content recorded is high (about 4 mg/kg wet weight), but the fact that the content of other heavy metals is in no way abnormal suggests that the Montedison waste products, which do not contain mercury, are not the reason for the death of this animal. The high mercury content may be attributable to the waste products of the chlorine industry discharged into the Gulf of Genoa and to the discharging at sea of the waste from mercury mines."

Furthermore, examination of the various foreign reports made on discharge locations in the North Sea or New York Bay lead to identical conclusions : no deaths of pelagic or even benthic fish (although such discharges are made at depths of 20 to 30 m) have been reported in the areas in question.

It seems likely that the macroscopic animals in the immediate vicinity of the waters where the effluents are most concentrated flee from them and thus escape the immediate toxic effect of the waste; the probability of macroscopic animals being directly engulfed in the waste discharges and affected by their acute toxicity is, moreover, likely to be low. Only additional

experiments could make it possible to establish, on the basis of an amount of data large enough to be statistically processable, whether or not the fish stocks have appreciably changed in the discharge area.

b) Behaviour of plankton in the discharge area

It will easily be understood that a study like this is difficult to carry out on the spot for purely technical reasons. It is therefore discussed in much greater detail in connection with the presentation of the results obtained in the laboratory: it should moreover be noted that plankton does not possess any means enabling it to flee from the discharge area: the laboratory study therefore gives an acceptable representation of the actual behaviour of plankton in the medium.

It is, however, worth while mentioning the conclusion of an American study made on the discharge of similar waste products in New York Bay.

The National Research Council of the National Academy of Sciences, Fish and Wildlife Service, mentions that ... "zooplanktonic organisms were immobilised by exposure to the effluent. But they generally resumed their activity and appeared normal after two or three minutes, even when remaining in the contaminated water.

Specimens placed in samples taken from the wash less than one minute after the passage of the lighter did not react. As soon as this water had been diluted half-and-half with uncontaminated sea water they reacted and started to swim about again".

It will be noted that these experiments carried out "in situ" do not provide any accurate experimental data (concentration, species observed ...), but they lead us to exclude any immediate large-scale mortality of zooplankton in the wash of the lighter which discharges the effluents into the sea.

Be that as it may, this study concludes that "the volume of acid water of each discharge is so small compared with the water available that the effects on the zooplankton and phytoplankton will be negligible".*

2) Experimental data on the behaviour of marine flora and fauna
with different concentrations of the effluent
Determination of acute toxicity thresholds

a) Report of the Institut Scientifique et Technique des Pêches
Maritimes

Measurements of acute toxicity were made on the following marine creatures:

1 phytoplanktonic alga	: Phacodactylum Tricornutum
1 zooplanktonic crustacean	: Artemia Salina
3 lamellibranch molluscs	: Ostrea Edulis (oyster) Cardium Edule (cockle) Mytilus Edulis (mussel)
1 gastropod mollusc	: Littorina littorea (winkle)
2 crustaceans	: Crangon crangon (shrimp) Palaeomon serratus (prawn)
2 fish	: Pomatoschistus minutus Elvers (post-larvae of Anguilla Anguilla).

The experiments were performed on lots of 10 animals in glass crystallisers with a capacity of 4 l, each of which received 2 l of solution. A suitable aeration was maintained by bubbling throughout the period of the tests.

The dead animals were removed and the cumulative mortality percentages after 48 and 96 hours were recorded.

* N.B. Translator's note: These two quotations, re-translated from the French version of the report in question, should be checked with the English original.

Results

The growth curves of *Phaedactylum tricornutum* for the different dilutions of the effluent are given in Fig. 1.

We find that the growth in the culture with a dilution of 1/10,000 is practically normal.

A dilution of 1/5000 shows a growth of approximately 65 % of the growth of the reference culture.

A dilution of 1/3000 corresponds very noticeably with the concentration which reduces the growth of the culture by half, or the LD 50.

Lastly, dilutions of 1/2000 and 1/1000 appear incompatible with the development of *Phaedactylum tricornutum*. But it would appear that the pH values of the cultures at these two dilutions are largely responsible for the absence of growth.

The cumulative mortality percentages after 48 and 96 hours are shown in Fig. 2.

We observe that the *Artemiae* show the greatest sensitivity, since 45, 50 and 100% of the population die at the dilutions of 1/3000, 1/2000 and 1/1000 respectively after 96 hours.

Shrimps and the two fish tested are also sensitive, because the dilution of 1/1000 causes the death of the whole of the populations after 96 hours.

Lastly, for *Palaemon serratus*, *Ostrea edulis*, *Cardium edulis*, *Mytilus edulis* and *Littorina littorea*, no mortality is found at the 5 dilutions tested.

We can therefore conclude that the effluent is acutely toxic

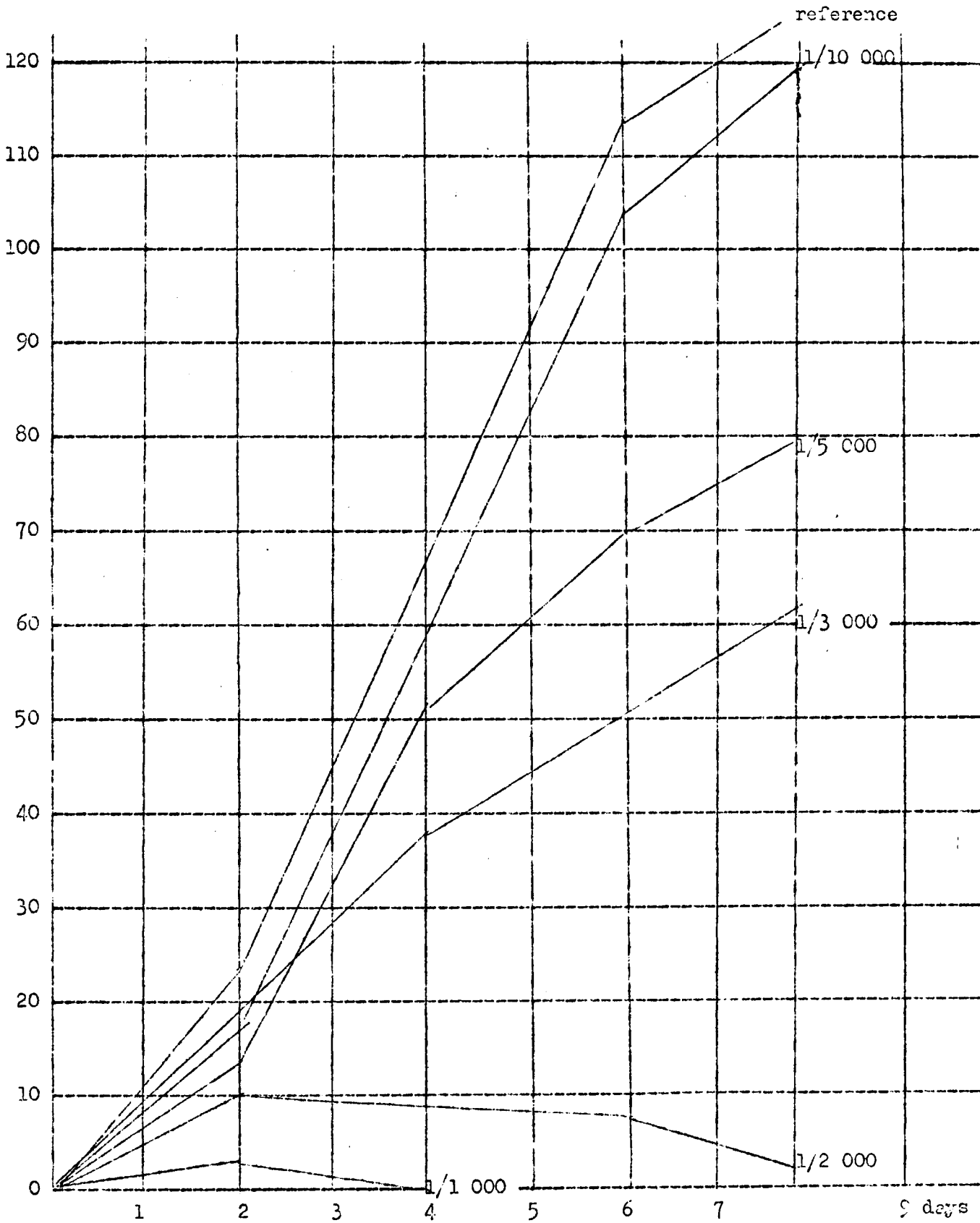


Figure 2 : Percentage mortality at 48 and 96 hours depending on the dilution of the effluent.

		1/10 000	1/5 000	1/3 000	1/2 000	1/1 000
<i>Artemia salina</i>	48 h	0	0	4	4	100
	96 h	0	16	45	50	100
<i>Palaemon serratus</i>	48 h	0	0	0	0	0
	96 h	0	0	0	0	0
<i>Crangon crangon</i>	48 h	0	0	0	0	66
	96 h	0	0	0	0	100
<i>Ostrea edulis</i>	48 h	0	0	0	0	0
	96 h	0	0	0	0	0
<i>Cardium edule</i>	48 h	0	0	0	0	0
	96 h	0	0	0	0	0
<i>Mytilus edulis</i>	48 h	0	0	0	0	0
	96 h	0	0	0	0	0
<i>Littorina littorea</i>	48 h	0	0	0	0	0
	96 h	0	0	0	0	0
<i>Pomatoschistus minutus</i>	48 h	0	0	0	0	100
	96 h	0	0	0	0	100
<i>Elvers Anguilla anguilla</i>	48 h	0	0	0	0	100
	96 h	0	0	0	0	100

for concentrations ranging from 1/5000 to 1/8000 (the latter concentration not being fatal to the organisms but retarding the growth of some of them).

b) Results provided by the Centre d'Etudes et de Recherches de Biologie et d'Océanographie Médicales (C.E.R.B.O.M.)

The work done by CERBOM revealed toxicity thresholds of the same order of magnitude as those observed by the I.S.T.P.M., i.e. varying toxicities for concentrations of 1/1000 to 1/10,000 (see the results below). It should be pointed out that the toxic dilution of 1/35,000 is recorded for the most sensitive fish, but after a stay of 10 days in polluted water, which represents artificial conditions.

Results

1. Pelagic type chain

- Phytoplankton : *Asterionella japonica* 1/1,000
- Zooplankton : *Artemia salina* 1/1,000
- Fish : *Carassius auratus* 1/2,000

2. Benthic type chain

- Marine bacteria : between 1/1,000 and 1/10,000
- Annelida : *Nereis diversicolor*: about 1/2,000
- Fish : *Labrus bergylta* 1/16,000

3. Neritic crustacean type chain

- For marine bacteria the thresholds had been determined during earlier experiments.
- Molluscs : *Mytilus edulis* : about 1/3,000
- Crustaceans : *Leander serratus* 1/2,000

4. Neritic mollusc type chain

- Phytoplankton : *Diogenes* sp 1/2,000 to 1/3,000
- Molluscs : *Mytilus edulis* 1/8,000

c) Foreign experiments

Interesting studies have been made in New York Bay by the Woods Hole Oceanographic Institution, Massachusetts.

Some of these give the following results of toxicity studies "in vitro" on copepoda and phytoplankton gathered close to the discharge area; the results are summarised as follows :

"The experiment on the development of phytoplankton did not show any significant effect on the growth of phytoplankton for a concentration of 1/10,000.

After 12 days both the culture in the dilute effluent and the reference culture showed an increase in the number of cells of the same order of magnitude, without any apparent change in the diversity of the species.

The studies of chlorophyll a and of carbon particles confirm the above results.

There does not appear to be any effect on the survival of the eggs or the development of the copepod "pseudodiaptomus coronatus" in solutions with concentrations of waste acid of 10^{-5} and 10^{-6} by volume. At these concentrations the period of development from the egg stage to the adult stage in filtered and unfiltered effluent was 13 to 14 days, whereas the reference in sea water (water from the Woods Hole bridge) indicated 13 days. In the same experiment, but with an acid concentration of 10^{-4} , the eggs did not hatch, high mortality of nauplii was observed, or the period of development from the egg to the adult was longer than that observed in the reference sample. Owing to the fact that the nauplii and the adults displayed, when examined, an accumulation of iron on their exo-skeletons and their appendages, filtered waste acid was used in another series of analyses during which the mortality and development times in each of the 10^{-4} waste acid concentrations and in the reference concentration were compared. In two of these solutions no copepod reached the adult stage.

In the two others the development time was lengthened from 3 to 7 days in comparison with the times observed to be taken to reach an identical degree of evolution in the reference sample from the Woods Hole bridge."*

* N.B. Translator's Note : Here too, compare this re-translation with the English original.

d) Acute toxicity thresholds

It is obviously difficult to draw any final conclusions from results of studies carried out on different organisms under conditions which are sometimes dissimilar; moreover, some figures put forward display relatively large discrepancies.

The results as a whole can, however, be summarised as follows :

- at a dilution of 1/10,000 the effluents display no toxicity or inhibition of growth in relation to the phytoplankton elements (all the results agree on this point);
- with regard to zooplankton, the toxicity threshold is for dilutions of 1/2,000 to 1/5,000. However, certain stages of development are sensitive to dilutions down to 1/100,000 (American experiment);
- for molluscs the results diverge and, in the worst case, give toxicities for a dilution of 1/8,000;
- for crustaceans, the toxic dilutions are around 1/2,000;
- lastly, the growth of marine bacteria is normal for a dilution of 1/10,000.

It can therefore be concluded that the direct toxicity effects of the effluent only appear below a dilution of 1/10,000.

3) Estimate of the direct consequences of the discharges on marine fauna and flora (The effect of sludge-type waste is excluded from the calculations)

It appears that a certain proportion of the "biomass" (total body of living matter) is affected by the direct toxicity of the waste products when these are insufficiently diluted. Part of the food stock of the zone in question can thus be affected.

It is risky to attempt to make a precise estimate of the annual loss of living matter due to the waste products; as has just been seen, the toxicity thresholds vary depending on the analyses made, and it is also necessary to make assumptions concerning the diffusion of the waste products, the primary productivity of the area, etc.

Nevertheless, it is possible to make the following estimates :

a) Phytoplanktonic productivity in the discharge area (primary productivity)

- b) The only data which we possess concerning the zone were published by Kondratieva (1970). Primary production was about 5 mg of carbon per m^3 per day at the surface, in March 1968. This value, with those of the other stations on the Ligurian Sea, is one of the highest that the author has been able to obtain from the various measurements which he has made throughout the Mediterranean. It seems, however, that Kondratieva's results are suspect in terms of absolute values.

It seems more reasonable to accept the figures of Minas (1968) relating to the Laboratory Buoy (42° 47' N, 7° 29' E). In these, annual primary production is estimated at 76 g of carbon per m^3 (aggregate production for the whole depth).

b) Estimate of the loss of primary productivity due to the direct effects of the waste products

On the basis of a discharge of 3,000 tonnes of effluents per day (or about 2,500 m³ with a density of 1.2) it is found that the volume necessary to dilute the effluent 10,000 times is 25,000,000 m³. (It was not possible to make allowance, in this estimate, for the screening effect of the sludge discharge.) In view of the fact that the horizontal rates

of diffusion are much higher than the vertical rates, it can be assumed that the thickness of the volume affected is less than 70 m (limit depth of the euphotic zone (1)). If it is assumed that in the 0 - 70 m zone primary productivity is independent of depth it will be seen that, for a depth of 70 m affected by the discharge, the surface area affected by insufficient dilution of the effluent is $360,000 \text{ m}^2$ or 36 hectares.

It is necessary to make an assumption here regarding the time which the waste products take to dilute down to the threshold of $1/10,000$: if we assume that in one day the medium reverts to normal conditions (and therefore that the waste products of the next day will be discharged into a zone which can be regarded as intact), it can be assumed that throughout the year 36 hectares will be permanently lost for the production of the zone.

Taking the primary-productivity figure adopted in section 3s), this represents a loss of :

$$360,000 \times 0.076 = 27,360 \text{ kg of carbon per year.}$$

If, furthermore, it is assumed (figures taken from Riley and Skirrow) that 10 grammes of biomass correspond to 1 gramme of organic carbon, we obtain a loss of primary productivity (phytoplankton) of 273,600 kg per year.

If, lastly, it is assumed that 1000 g of phytoplankton make possible the growth of 10 g of planktonivorous fish or of 1 gramme of carnivorous fish, this gives an annual loss of halieutic resources of the order of several hundreds of kilogrammes per year.

(1) Zone where photosynthesis occurs. A lens-shaped region of high productivity is located not far away from the zone. The depth of this would appear to be 150-200 m.

The argument is based on a number of parameters which are difficult to assess and are obviously arbitrary in nature. Even allowing for margin of error of about 10, it will be seen that the loss of nutritional resources due to the direct action of the waste products is extremely limited.

It must be recalled, however, it was not possible to take into account the role of the waste product discharged; it would certainly be negligible, in view of the presence of a high-productivity area close to the discharge zone.

Here more than elsewhere the number of assumptions involved calls for the greatest caution. Nevertheless, the low value of the figures obtained should be noted; it tallies with the results of the observations made at the site of the discharges in New York Bay, which lead to the conclusion that the loss of halieutic resources is negligible.

This judgment needs, however, to be qualified by "on the spot" observation of the effect of the discharges on local fishing, and by discussion - on the following pages - of the long-term effect of the waste products discharged from the point of view of accumulation phenomena.

SECTION II - THE LONG-TERM EFFECTS

We have already touched upon the importance from a physico-chemical point of view of the introduction of the heavy metals contained in the effluents.

We must now examine what are the possible biological consequences, of the accumulation of these elements along the food chains. These consequences can be studied in two ways :

- the first consists of the reproduction, in vitro, of phenomena of chronic poisoning;
- the second, more promising way consists of on-the-spot observation of the content of undesirable elements in animals fished or gathered in the geographical area of the discharges in order to draw conclusions as to the dangers entailed by their ingestion. This approach must allow for the extreme variability of the results obtained and be based on a sufficiently large number of analyses to bring out clearly the effect of the waste products themselves.

It would seem useful first of all to recall some data concerning the phenomena of concentration of the elements encountered in the effluents.

1) The "natural" accumulation processes

a.) The different contents observed in the natural medium

As has been emphasised elsewhere, titanium, chromium, vanadium and cadmium are naturally present in sea water, in extremely small proportions.

The natural traces of these elements are concentrated by certain organisms.

Thus the following contents have been observed in New Zealand bivalve organisms (Brooks and Rumsby, 1965, quoted by Horne).

Average content in ppm (ug/gramme) dry weight

	Scallop	Oyster	Mussel
Iron	2,915	680	1,960
Chromium	10	3	16
Vanadium	9	3	5
Cadmium	250	35	10

Similarly the following proportions are found in the flesh of certain marine organisms (ISTPM figures quoted in the GIPM report, 1973).

Contents in ppm (ug/gramme) dry matter :

- Chromium : fish : 0.02 to 1
- Cadmium : fish : 0.15 to 3
- algae: 0.0006.

Data concerning the content of titanium, vanadium and aluminium in marine organisms are more rarely found.

Information from C.E.R.B.O.M. mentions that :

"in the specialised literature it is assumed that for non-polluted fish, titanium and vanadium are not detectable; with regard to aluminium, the average proportions are of the order of 10⁻⁶ g/g dry weight of fish".

b) Toxicity of these different elements for human beings

The acceptable doses in foodstuffs are :

- 1 mg/kg of fish
 - 5 mg/kg in molluscs
- } for cadmium (fresh weight)

0.1 mg/kg in certain foodstuffs for chromium.

(ISTPM figures mentioned in the GIPII report.)

With regard to titanium and vanadium, there do not appear to be any national or international standards of toxicity. Furthermore, there are no results to be found of work concerning the toxicity of these two elements, which up to now have not been the subject of many publications.

Professor BRISON mentions, in a letter addressed to the CIESM and passed to us by the Chairman of the "Campaign against marine pollution" Committee of that international organisation :

"Titanium salts are in themselves harmless, since they are insoluble, with a few exceptions (bromides, chlorides, fluorides, iodides...).

The soluble salts are very unstable and rapidly decompose in the atmosphere. In the pure state, some of them are regarded as irritants, but this has nothing to do with the present subject. The most recent treatises on toxicology state that no case of poisoning by titanium or its salts is known. Titanium oxide is, as everyone knows, widely used for therapeutic purposes. It is administered in very heavy doses, several tens of grammes per day. Coirre titanium contains 9 g of titanium anhydride per 10 grammes and 2 to 3 doses per day, i.e. 30 grammes, are absorbed. "Bismutitane" contains 7.4 grammes of titanium anhydride and 2.5 grammes of bismuth sub-nitrate per 10 grammes; here again one or two doses are taken per day, making about 20 grammes. For my part I use these products a lot and make up many prescriptions for them.

Titanium oxide is included in the composition of many ointments, the best known being "Tétetitane". The sulphate mentioned (in

the letter from Mr. PAOLETTI (1)) is both insoluble and unstable, and the analyses presented in the Italian papers show that it has a high content of H₂SO₄ and iron sulphate, but obviously the sulphuric acid is immediately diluted and neutralised when it reaches the receiving sea water."

However, a document provided by CERBOM mentions that :

"Russian works have shown that ingestion of titanium (TiCl₃) in the organism of rabbits (2 mg/kg) led after a certain period (129 days) to certain metabolic disturbances. Other disturbances are produced by the ingestion of 0.05 mg/kg of TiCl₃. In the same document attention is drawn to metabolic disturbances resulting from excessive ingestion of vanadium."

2) Studies of accumulation and induced toxicity carried out in laboratories

a) Report of the I.S.T.P.M.

At the date of publication of the first report of the I.S.T.P.M. (February), only one short experiment on concentration phenomena had been performed; the animals surviving after four days in the effluents of different concentrations and the reference animals displayed no detectable differences in their content of iron and cadmium.

A much longer investigation (scheduled to extend over 3 to 4 months) is in progress: *Artemia Salina* will be grown from diatom cultures in an effluent diluted to 1/5000, and the *Artemia Salina* will itself

(1) An expert of the Italian scientific commission.

be used to feed shrimps and also fish. The results of this study will be known in June.

b) Results from CERBON

A. CONCENTRATION PHENOMENA

CERBON succeeded in measuring the phenomena of induced concentration by reconstituting in the laboratory four major alimentary chains of the ocean environment: the method employed consists of breeding the elements of the four chains in tanks containing variable dilutions of the effluents. Each alimentary stage which has thus possibly accumulated the undesirable substances from the waste matter serves as food for the higher stage, which itself is placed in a dilute solution of the effluent. Lastly the effect of the concentration phenomena on the final consumer (mouse) is tested.

The results reported by CERBON are as follows :

- "1) Neritic crustacean chain, consisting of micro-organisms, molluscs, shrimps (exposure to poisoning for 2 weeks for each of the components):
 - The molluscs (mussels) had titanium contents ranging from 2 to 4 $\mu\text{g/g}$ and vanadium contents ranging from 0.5 to 1 $\mu\text{g/g}$, whereas the reference samples had titanium contents below the detection limit and vanadium contents of around 0.1 $\mu\text{g/g}$, the concentration factor being 6 to 13 for titanium and 80 to 170 for vanadium, in comparison with the contents of the tested polluted water.
 - the crustaceans (shrimps) had contents of 5 to 7.5 $\mu\text{g/g}$ of titanium and 2.6 to 2.9 $\mu\text{g/g}$ of vanadium, whereas the reference samples showed no detectable content of titanium and contents of 0.5 $\mu\text{g/g}$ for vanadium, the concentration in comparison with the tested water being 16 to 25 for titanium and 430 to 490 for vanadium. (The degree of dilution of the effluent was 1/50,000.)

2) Benthic chain consisting of micro-organisms, annelida and fish which had lived in a tank in a 1/50,000 dilution of the effluent for one week in the case of the micro-organisms and annelida and for two months in the case of the fish:

- The annelida contained from 25 to 65 $\mu\text{g/g}$ of titanium and from 1.5 to 19.5 $\mu\text{g/g}$ of vanadium, whereas the contents of the reference samples were respectively 1 $\mu\text{g/g}$ of titanium and an undetectable proportion for vanadium. The concentration factor ranges between 400 and 1,000 for titanium and between 1,250 and 2,500 for vanadium in comparison with the contents of these metals in the tested water samples.
- The benthic fish (blennies) contained from 0.3 to 0.6 $\mu\text{g/g}$ - wet matter - of titanium and between 0.5 and 1.1 $\mu\text{g/g}$ of vanadium, while the reference samples' contents were below the detectable limit for titanium and 0.3 $\mu\text{g/g}$ for vanadium, so that the concentration factors in comparison with the polluted water were 5 to 10 for titanium and 400 to 600 for vanadium.

3) Pelagic chain composed of phytoplankton, zooplankton (exposure to poison for a period of 8 days) and fish (exposure for 15 days). Dilution tested : 1/10,000.

Titanium contents ranging from 6 to 16 $\mu\text{g/g}$ wet matter, and contents of 1.5 $\mu\text{g/g}$ of vanadium were observed in fish, whereas the reference samples showed no detectable content of either titanium or vanadium, the concentration ratios being of the order of 20 to 55 for titanium and around 250 for vanadium in comparison with the concentration of these metals in the tested water."

4) Meritic mollusc chain

The concentrations observed are not included in the results reported.

The results obtained at CERBOM thus confirm those mentioned in sub-section II-1) with regard to the possibility of accumulation of vanadium and titanium.

On the other hand, no indication was given by this organisation concerning the possible accumulation factors of chromium and cadmium.

- B. With regard to the induced toxicities observed in vitro, it should be noted that no phenomenon of this kind was found during CERBOM's experiments; while the same experiments performed on other industrial effluents (effluents of paper mills and of ceramics factories) had in fact led to the death of the final consumers (mice), no mortality was found at this stage by CERBOM, which concludes:

"No acute toxicity was found at the level of the final consumer after the successive consumption of the last stages of the four marine trophodynamic chains." The same document states, however: "although, in the medium term, there were no lethal manifestations in the land-based consumer, knowledge of the long-term effects of certain of its constituents does not exclude the possibility of delayed pathological manifestations".

3) Observation of the heavy-metal contents of the marine organisms collected in the discharge area.

We do not at present have many results of this kind. Only CERBOM reports on two series of analyses: the first concerns fish provided by the Veterinary Services Department of the Ajaccio Prefecture (the place where they were caught is not stated); the second concerns

fish sent by Bastia fishermen as having been caught north of Cap Corse. CERDOL remarks in this connection that it did not itself arrange for these two samples to be taken, which may introduce artefacts.

The results of these analyses are as follows :

FISH SUPPLIED BY THE VETERINARY SERVICES DEPARTMENT OF THE
AJACCIO PREFECTURE

Samples		Titanium	Vanadium	Aluminium
Sea bass	muscle	N.D.	N.D.	1.35
	intestine	N.D.	N.D.	6.35
	liver	N.D.	N.D.	9.36
	head	N.D.	1.33	6.30
Sea-bream	muscle	N.D.	N.D.	1.24
	intestine	N.D.	2.47	5.87
	liver	N.D.	N.D.	7.46
	head	N.D.	1.93	5.90
Bream	muscle	N.D.	N.D.	1.39
	intestine	N.D.	1.63	2.45
	liver	N.D.	N.D.	14.92
	head	N.D.	2.06	6.18

FISH PROVIDED BY BASTIA FISHERMEN AS HAVING BEEN CAUGHT
NORTH OF CAP CORSE

Samples		Titanium	Vanadium	Aluminium
Ray	muscle	N.D.	N.D.	1.79
	intestine	N.D.	N.D.	1.44
	gills	N.D.	N.D.	4.94
Sword-fish	muscle	1.50	1.50	110
Octopus	tentacle	8.45	N.D.	84.53

N.D. = not detectable.

It will be noted that titanium is not detectable in most of the samples, except for the sword-fish muscle and the octopus tentacle.

On the other hand, while all the edible parts of the animals (except for the sword-fish) contain no vanadium, relatively high contents of this element are found in the viscera and heads.

These first results may appear significant. It is extremely difficult, however, to draw any definitive conclusions from them.

A certain number of points require more thorough consideration:

- 1) The literature rarely contains contents by organs but rather average contents for each organism: the proportions of vanadium and titanium to be considered for a comparison with other results should therefore be corrected by averaging the results found in the viscera and heads with those for the muscles of the fish.
- 2) Moreover, it is rather difficult to explain the high aluminium contents found in the different organisms; there is usually little information available on the concentration factors of this element, which incidentally does not appear in very large quantities in the effluents.
- 3) As has already been emphasised, there is at present a shortage of overall data on the actual toxicities of titanium and vanadium. It would therefore be useful, as a first stage, to examine the proportions of cadmium and chromium contained in marine organisms, as the contents of these elements have already been the subject of detailed investigations leading to the establishment of standards; knowledge of the contents of titanium and vanadium, while interesting in itself, does not at present enable one to estimate the possible dangers of consumption of marine products, owing to the lack of reference data on the proportions contained in animals collected in unpolluted areas of the Mediterranean.

N.B. Further results were reported by CERDOM in a communication dated 18th April 1973.

... "but, furthermore, at the request of the Veterinary Services Department of the Prefecture of Corsica, we have carried out a series of measurements on fish caught off Corsica which have been sent to us regularly for the last few weeks. These samples enabled us to find average values of 0.42 titanium, 0.51 for vanadium and 0.40 for mercury (microgramme/gramme - wet weight).

This study is in progress at present. We shall keep you informed of the results obtained subsequently.

The following two points may be noted :

- 1) The titanium contents are higher than previously, while the vanadium contents, presented as average values, correspond to the previous values.
- 2) The mercury contents, although high, remain below the acceptable thresholds. In view of the fact that there has never up to now been any report of the presence of mercury in the effluents, it appears difficult at present to link the contents observed with the Italian discharges."

SECTION III - ECOLOGICAL ASPECTS - CONCLUSION

The analysis of the scientific and bibliographical data compiled in an effort to gain a clearer idea of the details and effects of the waste products discharged by the Montedison company enables us to draw some conclusions.

The industrial waste products in the sea display an appreciable direct toxicity due to their acidity and their iron content, which causes, in the wake of the discharging vessel, i.e. in a limited volume of water, the disappearance of the species which are unable to flee or which cannot withstand 1/10,000 dilutions of the effluent in the medium (this being the threshold value obtained for prolonged stays); plankton is probably the main victim of this mode of poisoning, although the estimate of the quantities per day affected by the waste products results in low values when measured in the Ligurian Sea.

It has not so far been possible to demonstrate the residual toxicity of these waste products, i.e. the harmfulness which may result in the long run from the systematic introduction into the medium of the heavy metals which they contain. Chemical analysis of the waste products has shown that they did in fact contain small proportions of residual toxic substances. The studies carried out in vitro have enabled the possibility of accumulation of these substances along the alimentary chain to be demonstrated. Furthermore, the presence of residual elements in certain fish taken from the discharge area would appear to confirm this observation, although responsibility for the presence of these substances in the animals collected cannot with absolute certainty be attributed to Montedison's waste products. It should moreover be recalled that it has not been possible to date to prove the chronic toxicity of the substances contained in Montedison's industrial waste products even in the laboratory.

However, in view of the absence of definite conclusions on this point, vigilance is called for until such time as the organisations which are at present still engaged in long-term experiments make known their results.

CONCLUSIONS

CONCLUSIONS

The production capacity of titanium dioxide factories in Europe of the Nine is 840.000 tonnes per year (tpa). This represents 39% of world capacity (2 175 000 tpa) and is divided up as follows :

- 741 000 tpa (88%) for the sulphate process
- 99 000 tpa (12%) for the chlorine process.

Factoring discharging into the Channel or the North Sea account for 727 000 tpa (87%) and factories discharging into the Mediterranean account for 50 000 tpa (6%). Two factories (63 000 tpa, or 7%) treat their waste on land.

At present, discharge levels are as follows :

(1) in the North Sea and the Channel, either in estuaries or on the open sea :

- 4 100 t/day SO_4H_2 expressed as 100% concentration
- 3 000 t/day $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (ferrous sulphate)
- 1 300 t/day FeSO_4 discharged with the "acid waters" (SO_4H_2)

(2) in the Mediterranean :

- 335 t/day SO_4H_2 expressed as 100% concentration in the form of neutralized products (2 600 t/day)
- 580 t/day $\text{Fe SO}_4 7\text{H}_2\text{O}$ are at present stored on land.

A whole series of ecological pollution monitoring campaigns have been carried out in the actual discharge areas ; these campaigns have been investigated by the national authorities or sometimes by the manufacturers themselves.

It is clear from an analysis of the results of these controls that waste from the TiO_2 industry is potentially or actually harmful. These adverse effects on the marine environment are due above all to acidity, the presence of ferrous sulphate and probably other metals (heavy metals).

The effects in question can take the following various forms, depending on the method and place of dumping :

- (1) reduced oxygenation and pH of the water and increased concentration of Fe and heavy metals ;
- (2) (a) temporary shortage of the zooplankton biomass and inducement of effects leading to a deterioration of the morphological structure of its components ;
(b) repulsion and loss of some species of fish ;
(c) reduction of the biomass, production and specific diversity of benthic and/or nectobenthic biocenoses in the discharge area. In more severe cases, all animal life may disappear .
- (3) change in the colour, transparency and turbidity of the water and temporary reduction of photosyntheses, of the phytoplankton and of primary production, particularly in the case of surface dumping. The seabed becomes covered with iron oxides and the oxides of other metals where the dumping is carried out in estuaries and in shallow water ;
- (4) on the other hand, there is no evidence of any toxic effects on man from the consumption of species of fish caught in the discharge areas.

Part 1 of this report contains an inventory of the waste from the production of TiO₂. These wastes have been classified into four major categories corresponding to the waste products discharged by factories at different stages of production. These categories are :

1. insoluble matter remaining after filtration
2. "copperas" (ferrous sulphate)
3. strong acids
4. weak acids or weak liquors.

It would seem fair to suggest that industries in this sector should, within certain reasonable time limits :

- a) store on land the insoluble matter remaining after filtration ;
- b) make certain reductions in the total pollution (either 30%, 70% or 95%).

These reductions are based on perfectly feasible techniques. For plants using Ilmenite for example, a reduction of

30% would mean that the ferrous sulphate has been treated,
70% that the ferrous sulphate and the strong acids had been treated, and
95% that the ferrous sulphate, strong acids and the bulk of the weak acids
had been treated.

The report is also considered how and at what price this waste could be disposed of either by conversion or recycling (see p. 28 and following).

It should be borne in mind that the processing cost values date back to the end of 1973 and the beginning of 1974 and must be updated to take account of changes in the economic situation. A study on this is being carried out ; however, the figures given in the report remain valid for the purpose of assessing the high cost of treatment in relation to production costs and for comparing the various solutions proposed.