

environment and quality of life

World TiO₂ industry projects and their environmental impact

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TiO₂ INDUSTRY PROSPECTS

During the last years, the titanium dioxide industry has been subjected to a kind of uncertainty due to a lot of factors.

In the early 70's, technical aspects prevailed but presently economic and political aspects are the main elements of decision.

TiO₂ producers, environmental authorities and raw materials producers are three independent groups. Each of these three groups has to take into account the possible actions by the other two groups.

A more detailed analysis of the situation of the years 76-77 shows an evolution of the TiO₂ production processes.

The sulfate process could use richer raw materials. Presently the main grades of R-materials are 45% - 54% - 72% (TiO₂) but it should be possible to use at least as an additional feed, R-materials like African slag which contains about 85% TiO₂ or even richer grade like synthetic rutile which could contain 92% TiO₂ (Benifite-S or Murphyores).

However it must be noted that the use of rich R-materials can be explained by economic reasons (chemical consumption and investment) but the overall amount of effluents is not very significantly reduced and the amount of free acid in the waste stream is about the same. The amount of salts is reduced but some salts which are left in can hinder the recycling processes.

As far as the chlorine-process is concerned, here is a tendency to use R-materials of lower grade.

African slag has not been tested on an industrial scale but it must not be neglected.

On the other hand, some companies, like Kronos Titan in Leverkusen (RFA), claim that they can operate on an industrial scale a chlorine process using low grade R-material.

The range of raw materials, which can be used for the sulfate and chlorine processes is becoming wider and wider.

However it must be noted that the economic use of such raw-materials requires special design features which are more easily implemented in new plants.

The incentives which led the producers to develop these processes are the following :

- access to a wide variety of available raw materials so as to ensure reliable and economics supplies

- optimization of the raw materials cost as a function of the market and of the plant sites
- reduction of the amount of effluents to dispose of a by-products to market

Preliminary economic calculations have shown that even if the environmental aspects are not taken into account the use of richer ore can be justified by the savings on other chemicals and on capital cost.

An overcost attached to the environmental factor could make their productions workable.

As far as enriched raw materials are concerned it can be noticed that :

- several synthetic rutile processes are available (Benilite, Western titanium, Ishihara, Murphysores, S.K.) and the first three have been operated on an industrial scale.
- several S. Rutile plant are already in operation and some other are under construction. These plants represent a capacity of about 400 000 tpa
- 400 000 tpa of African Slag (85% TiO_2) will be produced by the end of 1978

If such a slag can be used in chlorine processes, it could become a major competitor of the rich raw-material used up to now. At this stage natural Rutile could be partially replaced by two competing contenders : synthetic rutile and slag (85% TiO_2).

For long-range planning, it must be noted that on the one hand the minimum production cost of synthetic rutile is about 160 UC/t (end 76) and, on the other hand, the extension of the rich R-materials market could make large scale mining operation attractive because of their lower cost of production.

Up to now the small market elasticity has been such that these kind of operations were not very attractive.

Various methods have been developed in order to select the best possible sites :

- synthetic rutile production near Mineral production (Malaysia- Australia)
- synthetic rutile production near an HCl source. In this case Ilmenite is imported, and S. Rutile is exported (Taiwan)
- synthetic rutile production near the pigment plant (Japan : Sakai). In this case Ilmenite is imported
- synthetic rutile production near Mineral production with local development of pigment industry (India).

Each of these sites have been chosen with according to specific local conditions which must not be generalized.

Selling pigment requires a very important technical and commercial assistance and new producers can come across quite a few difficulties when entering an established market.

It seems that India, for example, would be more interested by the marketing of the pigment in the developing countries.

The location of Synthetic rutile plants near pigment production could be more justified by political reasons than by economic reasons. Such a location allows a good production control and a wider choice of readily available ilmenite.

Finally it must be noted that the sizes of Synthetic rutile and pigment plants are of the same order of magnitude.

This factor would allow some joint-venture agreements to be signed.

Taking into account the environmental factors, there is a very definite evolution, especially in Japan where the regulation, published in 1971, are such that in most cases a complete treatment is required.

Dumping in the sea is quite exceptional and very limited in time and quantity.

The Japanese solutions cannot be considered as universally applicable nevertheless it shows how this industry adapted its operations to the local context.

The treatment used can be as simple as a rough neutralization, but in some cases it is much more sophisticated. These treatments are used in new plants as well as in old plants.

In the USA the overall situation is not so clear but some important realizations reveal a significant trend. One plant (American Cyanamid) operates with a complete treatment and the effluent quality of this installation will be used as a basis for the preparation of effluent standards. Other plants (Glidden Durkee) have only a partial treatment but it is planned to complete these facilities.

The Chlorine based Du Pont plant uses low grade ore and the effluents are dumped in deep well or in the sea but Du Pont has developed different ways to deal with the Iron chlorides.

In Canada, the most recent realizations are concerned with the treatment of gaseous effluents, however the liquid effluents are still dumped in the river. Regulations, very similar to their American counterparts are in preparation.

In India, a new producer (Kerala Minerals) plans to use the synthetic rutile process and the chlorine route.

Another producer which uses the sulfate process is analysing the possibility of producing ammonium sulfate from his effluents.

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SECTION 1

TiO₂ PRODUCTION

SECTION 1TiO₂ PRODUCTION

1-1 Technical features

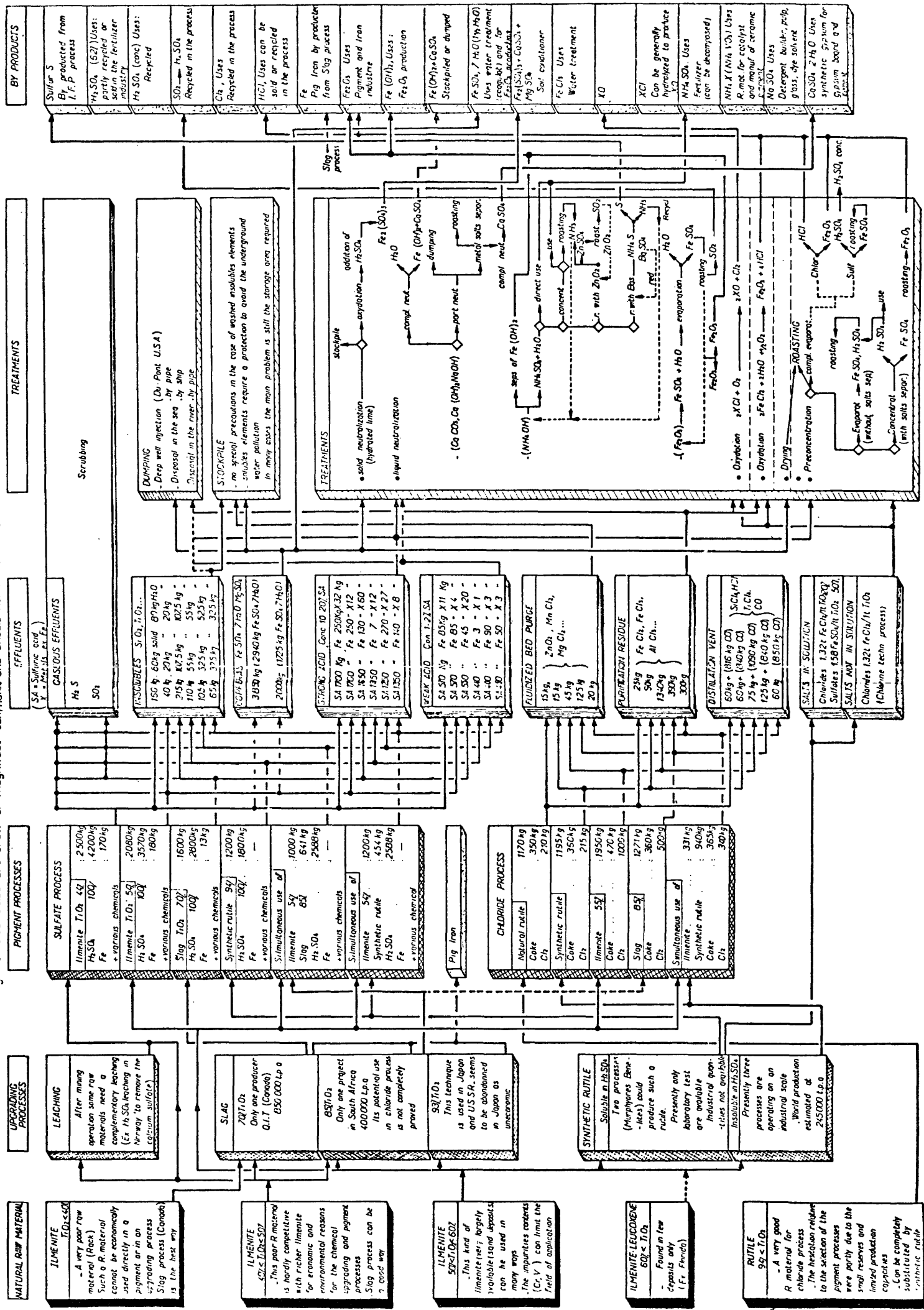
- 1-1-1 Overall technical pattern of TiO₂ industry
- 1-1-2 Description of possible routes with recycling
- 1-1-3 Raw material input and effluent output for different minerals

1-2 Economical features

- 1-2-1 TiO₂ consumptions
- 1-2-2 TiO₂ price
- 1-2-3 TiO₂ trade

OVERALL TECHNICAL PATTERN OF TiO₂ INDUSTRY

... magnitude estimates and should not be taken as a basis for a material balance)



1-1 TECHNICAL FEATURES

1-1-1 Overall technical pattern of TiO₂ industry

The main routes which could be considered for the TiO₂ industry are shown in a single figure (figure 1-1).

These routes have been drawn without any preconceived ideas of their economic advantages.

It must be noted that the quantities of Raw materials and effluents which are listed in this figure are only order of magnitude estimates and should not be taken as a basis for a material balance.

Concerning the simultaneous use of different raw materials, it can be done by mixing them but only within narrow limits it can also be done by the management of the raw materials used successively. This management could only concern the sulfuric digestion or the chlorination step.

The different quantities are referred to the production of one ton of TiO₂ pigment.

1-1-2 Description of possible routes with recycling

As the Ilmenite is the only raw material largely available all these processes use ilmenite.

For each cycle we have calculated the complete raw material and utilities consumptions and the amount of by-products.

In order to compare the different energy contents of these cycles, we have converted the utilities consumption to an equivalent fuel consumption.

The bases of this equivalence are :

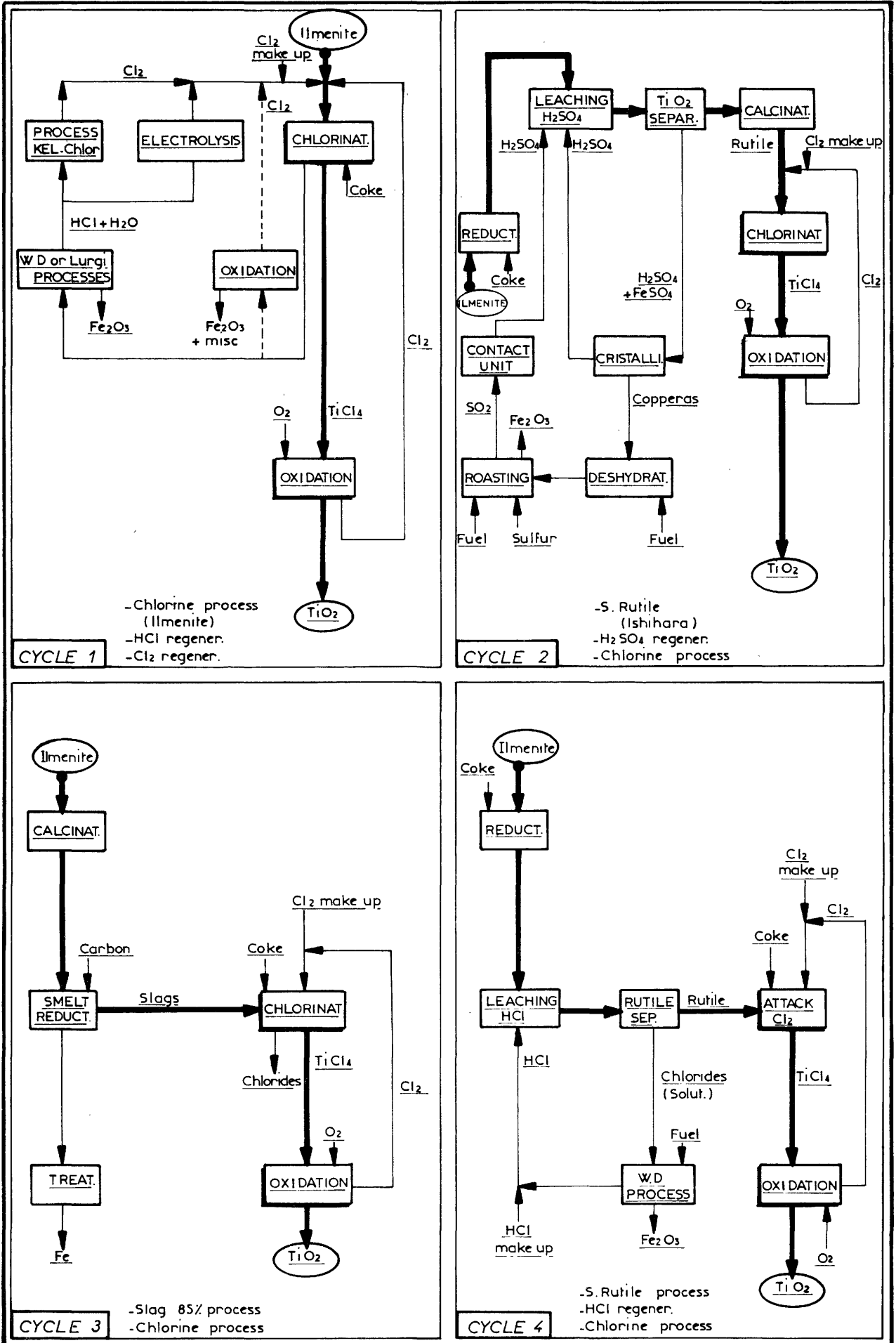
- Electricity 1kwh	=	0.297 kg fuel
- Steam	=	77.0 "
- Cooling water 1m3	=	0.074 "
- 1t of chlorine 3650 kwh	=	1,084.0 "
- 1t of oxygen	=	236.0 "

A - Routes based on the chlorine process

Cycles 1 - 2 - 3 - 4 (figure 1-2)

We have considered four cycles based on the chlorine process.

CYCLES BASED ON CHLORINE PROCESS



CYCLES BASED ON CHLORINE PROCESS (Raw material and utilities consumption)

	CYCLE 1						CYCLE 2						CYCLE 3			CYCLE 4		
	Pigment process	Chlorides (luml)	Chlorine regeneration	Totals	Fuel equivalent	Upgrading process	Coppers drying	Roasting	Contact unit	Pigment process	Totals	Fuel equivalent	Upgrading process	Pigment process	Totals	Fuel equivalent		
R. MATERIAL †																		
Ilmenite (t)	2.0			2.0		2.2				1.2	2.2		2.017	1.2	2.017		2.017	
S. Rutile (t)						0.95												
H ₂ SO ₄ (t)																		
HCl (t)	1.03		0.754	0.3						0.25	0.25		0.055	0.25	0.055		0.055	
Cl ₂ (t)	0.41		0.169	0.58						0.40	0.40		0.40	0.40	0.40		0.40	
Oxygen (t)	0.48		0.026	0.48						0.36	0.47		0.36	0.36	0.36		0.36	
Coke						2.89												
FeSO ₄ 7H ₂ O							1.75											
FeSO ₄ 15H ₂ O							0.065		0.64		0.065							
Sulfur (t)																		
miscell (t)																		
SO ₂																		
FeCl ₃ FeCl ₂		1.38		0.026														
UTILITIES																		
Elect. Kwh	1,248	231	40	2,300	0.683	330	45	45	45	749	1,927	0.572	429	749	1,178	0.350	1,178	
C. Water m3	38	5.0	25.6	69	0.005	27	31	31	31	23	81	0.006	13.2	23	36.2	0.003	36.2	
Steam (t)																		
Fuel (t)	0.166	0.150		0.316	0.316	0.400	0.13	0.1	0.1	0.1	0.78	0.780	0.596	0.1	0.696	0.696	0.696	
Frigor(kwh)	780							469										
Equivalent. Fuel					1.004†							1.358					1.049†	
TOTALS																		
PRODUCTS †																		
S. Rutile (t)				1.00		1.2				1.00	1.00		1.1	1.00	1.00		1.00	
Pigment (t)	1.00									0.09	0.09			0.09	0.09		0.09	
FeCl ₃ , FeCl ₂	1.38									0.015	0.015			0.015	0.015		0.015	
CaCl ₂ , MgCl ₂	0.046			0.046						0.9	0.9			0.9	0.9		0.9	
SiCl ₄ + CO	1.195			1.195														
Cl ₂			0.73															
HCl (100%)		0.754																
Fe ₂ O ₃		0.7		0.7														
FeSO ₄ 7H ₂ O																		
FeSO ₄ 15H ₂ O						2.89												
SO ₂							0.64											
Chlorides(sol)																		
Fe																		
H ₂ SO ₄							0.95											

* Frigorics are expressed in equivalent kwh

CYCLE 1

Description The main steps of this process are :

- complete chlorination of the Ilmenite
- separation of titanium tetrachloride from the other metal chlorides
- oxidation of $TiCl_4$ so as to produce TiO_2 pigment and recycling on the combined chlorine.
- Treatment of the metal chloride.

This treatment can be :

- . a direct oxidation of the chlorides with regeneration of the chlorine combined and production of metal oxides (mainly Iron oxide)

or

- . a hydrolysis of the metal chloride in HCl and metal oxides
- . a regeneration of Cl_2 from HCl by electrolysis or oxidation (Deacon process)

The main by-products are :

- . gaseous effluent from the chloride process
- . metal oxides
- . some minor effluents from the Deacon process

Main consumptions

The main consumptions of the chloride process are established by a material balance ; whereas utilities consumptions are computed by assuming that the figures are proportional to the molar quantities.

The utilities consumptions in the hydrolysis process are calculated by means of a material balance and with the Woodall Duckham figures.

The main consumption of the oxidation of HCl are based on the figures published by Kellogg for the Kel-Chlor process.

Balance Detailed figures and totals are shown in table 1-1 "Cycle 1".

CYCLE 2Description

The main steps of this process are :

- ilmenite upgrading, which can be broken down as follows :
 - . reduction of ilmenite
 - . Leaching (H_2SO_4)
 - . separation of Copperas
 - . Dehydration and roasting of copperas
 - . recycling of SO_2 % SO_3 and H_2SO_4
- chlorination of the S. Rutile
- Oxidation of $TiCl_4$ with Cl_2 recycling

Main consumptions

The consumptions of the upgrading process are based on figures corresponding to the Ishara S.K. process.

The consumptions of the Copperas treatment process are based on figures from Lurgi.

We have considered that the consumption of the chloride process are the same as those of the chloride process (natural rutile based).

CYCLE 3

Description

The main steps of this cycle are :

- treatment of the raw ilmenite by the slag process with :
- complete chlorination of the slag
- separation of the $TiCl_4$
- oxidation of $TiCl_4$ with recycling of Cl_2

(NB : In this case the amount of miscellaneous metal chlorides issued from the chlorination step is low and could be converted for use).

Main consumption

As there is no precise figures available for the production of slag (85% TiO_2) we have not done any calculation for this cycle.

CYCLE 4Description

The main steps of this process are :

- ilmenite upgrading, which can be broken down as follows :
 - . ilmenite reduction
 - . leaching (HCl)
 - . separation of metal chlorides
 - . hydrolysis with recycling of HCl to the leaching step and production of metal oxides
- chlorination of the S. Rutile
- Oxidation of $TiCl_4$ with Cl_2 recycling

Main consumptions

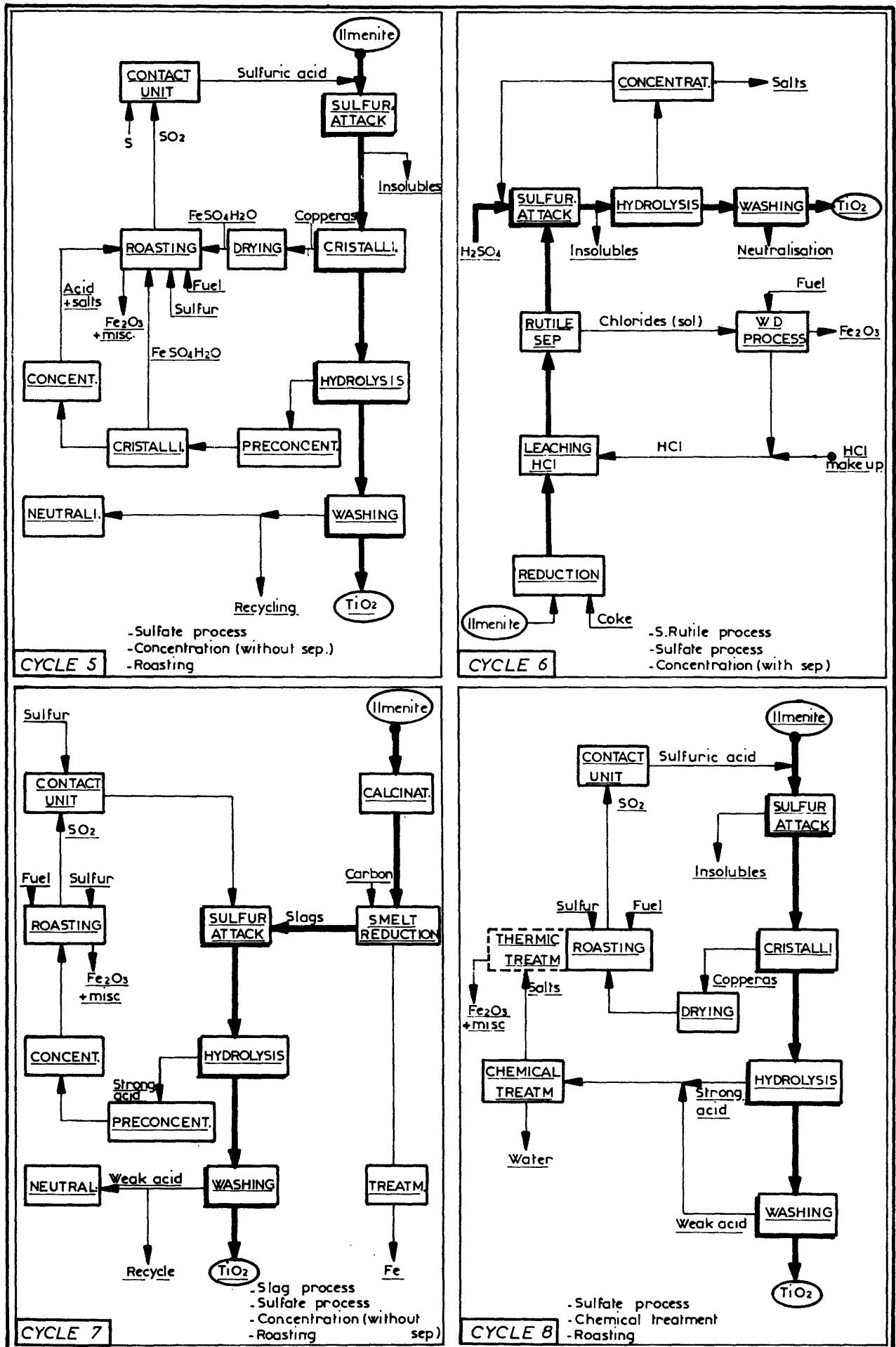
The main consumptions of the upgrading process are established with figures published by Benilite Corp of Am.

The consumptions of the chloride process are considered as being the same the data of the natural rutile based chloride process.

Balance

Detailed figures and totals are given in table 1-1 "cycle 4".

CYCLES BASED ON SULFATE PROCESS



CYCLES BASED ON SULFATE PROCESS (Raw material and utilities consumption)

TABLE 1-2

	CYCLE 5					CYCLE 6					CYCLE 7					CYCLE 8					Totals			
	Pigments	Drying	Concn.	Roasting	Contact Unit	Totals	Fuel equivall.	Slag	Pigments	Concn.	Roasting	Contact Unit	Totals	Fuel equivall.	Pigments	Drying	I.F. Process	Roasting	Contact Unit	Totals		Fuel equivall.		
R. MAT.	2.00					2.20	3.50						3.50		2.00					2.00				
Ilmenite						2.20							3.50		2.00					2.00				
S. Rutile						0.15							0.30		3.50					0.04				
Sulfur	3.50					1.8							1.23					0.9 (+0.04)						
H ₂ SO ₄						0.06							0.500						2.33					
SO ₂						0.15							0.01											
HCl(100%)						0.10		0.500					Acid Conc											
Coke	0.10					0.15		0.01					0.01											
Iron	2.00					0.15		0.15					0.15		2.00									
FeSO ₄ ·7H ₂ O						8.2		9.0					1.2		9.75									
FeSO ₄ ·H ₂ O						0.15		0.15					0.15		33.70									
Li Acid						0.15		0.15					0.15											
7. Acid						0.15		0.15					0.15											
Miscell.						0.15		0.15					0.15											
UTILITIES																								
Elec(kwh)	1,040	110	80	172	170	360	1,000	60	30	1,450	0.430	5,920	1,000	74	135	136	135	136	170	1,371	2,157	1,040	0.407	
C. Water	52		260		115	427	0.031	14.4	15	320	0.024	50	245	50	92	92	92	92	115	1,167	0.028	52	0.013	
P. Water	0.710	0.070	0.530	0.917	0.917	0.65	0.70	0.492	-0.5	1.84	1.840	0.70	0.50	0.72	-2.9	-2.9	-2.9	-2.9	-3.6	1.99	1.92	0.71	1.99	
Fuel(t)						2.23	2.230			-0.5	-0.5	-0.200								-9.5	0.14			0.758
Steam (t)						-3.6	-0.200														-13.1	-0.168		
Frigor(kwh)																								
Equal. Fuel TOTALS						2.531				2.321					3.941						1.650			
PRODUCTS																								
Pigments	100					100				100					100					100				
Rutile						1.2				1.6					0.04					0.04				
Chlor. sol						0.04				0.20					0.20					0.04				
Insolubles	0.04					0.04				0.20					0.20					0.04				
Copperas	2.00					1.35	0.45			1.65					1.70					2.00				
St. acid SA	1.70					0.07				0.13					0.25					1.70				
to roast.						6.8				7.20					7.80					2.00				
Fe	0.25					0.44				0.55					0.57					0.25				
H ₂ O	7.80					0.03				0.045					0.09					7.80				
W. acid SA	0.57					22.0				30.00					33.00					0.57				
Fe	0.09					1.2				1.2					1.2					0.09				
H ₂ O	33.00					3.5				3.5					3.5					33.00				
FeSO ₄ ·H ₂ O						1.56				1.56					2.33					1.56				
H ₂ SO ₄						0.90				0.90					0.90					0.90				
SO ₂						0.80				0.80					0.80					0.80				
sulfur						1.93				1.93					1.93					1.93				
Fe ₂ O ₃						0.95				0.95					0.95					0.95				
Fe						1.11				1.11					1.11					1.11				
neut. prod.						0.95				0.95					0.95					0.95				

B - Routes based on the sulfate process

Cycles 5-6-7-8 (figure (1-3))

We have considered four cycles based on the sulfate process with complete treatment :

CYCLE 5	CYCLE 7
CYCLE 6	CYCLE 8

CYCLE 5Description

This cycle is based on the sulfate process with ilmenite as raw material.

The main steps of this process are :

- Copperas drying and roasting with production of Fe_2O_3 and SO_2 . SO_2 oxidized to produce SO_3 then H_2SO_4 .
- strong acid concentration with separation of salts. Strong acid is then roasted with copperas
- Weak acid neutralization

In this process the iron part of the ilmenite is obtained as Fe_2O_3 and sulfuric acid is recycled. Only a few part of the weak acid stream is neutralized as neutralization products.

Consumptions

The main consumption relative to the treatment are based on Lurgi information (Lurgi had indeed considered such a way).

By-product

The iron part of the Ilmenite is obtained as Ferric oxide whereas sulfur is recycled as SO_2 , SO_3 , and finally H_2SO_4 .

CYCLE 6

Description

This process is based on the sulfate process with synthetic rutile (soluble in sulfuric acid) as raw material.

The main steps of this cycle are :

- the main steps of the synthetic R process (Benilite S or Murphyoeres)
- the main steps of the sulfat process
- strong acid concentration with the separation of salts
- weak acid neutralization

It must be noted that in this case, the strong acid contains only few impurities, it is necessary to have a purge on the recycled sulfuric acid in order to maintain the quality of the final product. Sometimes it may be more economical to sell a part of the strong concentrated acid at a lower concentration.

Consumption

The main consumptions relative to the upgrading process are the same as the Benilite figures, considering that the production of sulfuric acid soluble synthetic rutile does not modify consumption notably.

CYCLE 7Description

This cycle is based on the sulfate process with slag as Raw material.

The main steps of this cycle are :

- Raw ilmenite treatment by the slag process with :
 - . Separation of the iron as molten pig iron
 - . production of slag (70% TiO_2)
- The main step of sulfate process
 - . strong acid concentration and roasting with production of SO_2 which is converted in SO_4 and H_2SO_4 for recycling
 - . neutralization of the weak acid

Consumptions

- consumptions relative to the treatment steps are based on Lurgi information

by-products

The iron part of the ilmenite is obtained as Fe_2O_3 whereas sulfur is recycled as SO_2 , SO_3 and H_2SO_4 .

CYCLE 8

Description

This process is based on the sulfate process with ilmenite as raw material.

The main steps of this process are :

- the main steps of the sulfat process
- strong an weak acid chemical treatment which yields a solid compound which can separated from water
- regeneration of this compound with production of a chemical compound of sulfur

Consumption

Consumptions relative to the treatment steps are based on the I.F.P. process in which acid in neutralized by Ammonia and a regeneration cycle is implemented.

By-product

The iron part of the ilmenite is obtained as Fe (OH)_2 whereas the sulfur content of the waste sulfuric acid is obtained as sulfur.

1-1-3 Raw material input and effluent output for different minerals

A - Sulfate process

Minerals

Presently the sulfate proces raw material can be put into three categories :

- . low grade ilmenite (40-50% TiO_2)
e.g. : Norwegian ilmenite
- . Av. grade ilmenite (50%-60% TiO_2)
eg : Australian ilmenite
- . slag (70% TiO_2)
eg : Canadian slag

In the future two other categories of raw material will be available :

- . slag (85% TiO_2)
e.g. Richard Bay slag
- . synthetic Rutile (94% TiO_2)
e.g. : S. Rutile from Benilite S. process
or Murphyoeres proc.

The use of Richard Bay Slag adds some difficulties (e.g gaseous emissions) but these difficulties have been already considered for the canadian slag and the techniques can be improved.

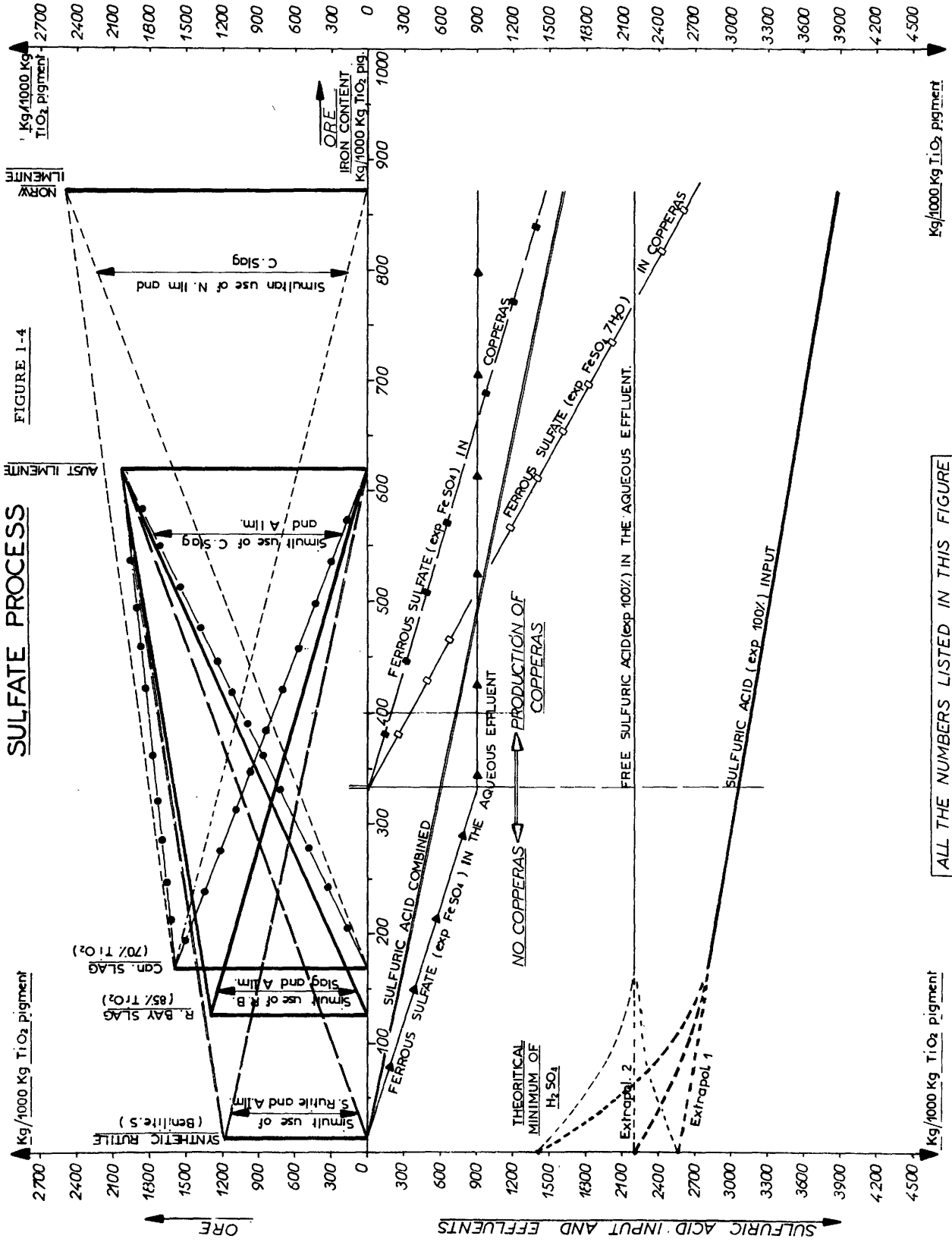
There is some doubt concerning the use of synthetic rutile in the sulfate process but many laboratory tests has been already carried out (see Annex p A-23).

Simultaneous use

A part from these five raw material categories we can add the possibility of using mixtures or using simultaneously various raw materials.

The direct mixing of minerals before the digestion step is limited for the following reasons :

RAW MATERIAL INPUT AND EFFLUENT OUTPUT FOR DIFFERENT ORES



- the solid handling is more extensive
- the conditions of digestion of different minerals are also different and in some cases a part of the the mixture remains undissolved. It seems that for a given mineral and for the corresponding digestion conditions is only possible to add about 5% of an other mineral without important modification of these conditions

These limitative reasons must not completely exclude the possibilities of simultaneous use. The sulfate process is a semi continuous process and it is possible to optimize the combination of minerals and digestion liquors. Mixing of digestion liquors might allow the user to adjust the iron content of the overall mixture before the hydrolisys step. A very large range of mixture could be produced this way.

This is the reason why we have shown in figure 1-4, the main categories of mineral and the possible mixtures. In this figure, it is possible to determine the amount of each mineral in the mixture for a given iron content referred to the production of 1 ton of TiO_2 .

Sulfuric acid consumption and effluent output

The quantities shown in figure 1-4 must only be considered as order of magnitude.

The horizontal scale is the Iron contained in the amount of mineral necessary for the production of 1 ton of TiO_2 .

The upper vertical scale is the amount of Minerals necessary for the production of 1 ton of TiO_2 . This amount is a function of the mineral type. The diagonal lines correspond to the cases of simultaneous use.

The lower part of the figure corresponds to the total sulfuric acid input, the free sulfuric in the waste acid (strong acid and weak acid), the ferrous sulfate in the copperas.

The vertical line drawn at the abscissa 330 divides the plane into two regions

- . left hand side : no copperas production
- . right hand side : copperas production

B - Chloride process

Minerals.

Presently the suitable raw materials for the chloride process can be divided in three categories :

- Natural rutile (96% TiO_2)
- Synthetic rutile (about 94% TiO_2)
- Mixture of rutile and leucoxene (about 70% TiO_2)

In the future two other categories of raw material will be available :

- Richard Bay slag (85% TiO_2)
- Ilmenite (55%-65% TiO_2)

We will not discuss in this chapter the economic position of these different raw material

. Richard Bay Slag

There is some doubt concerning the use of Richard Bay slag in the chloride process, and the feeling of the producers is very qualified :

- only small samples of R. Bay slag were available and were not big enough to run industrial tests (continuous)

- the Canadian slag is not suitable for the chloride process because its CaO content
- The Richard Bay slag, produced from South African ilmenite, will contain less detrimental impurities due to the quality of this type of ilmenite
- Russian chlorinates slag (83%) (Zaporozhe)

. Ilmenite

The total chlorination of ilmenite has been widely studied, but presently only few companies have a complete process. Du Pont is already running plants using a mixture of Leucoxene and Rutile whereas Kronos Titan (N. Lead) has announced the completion of such a process.

Chlorine consumption and effluent output

As the previous one, the figure 1-5 shows Raw material consumptions and the order of magnitude of effluents.

We have again considered the possibility of mixing minerals.

The lower part of the figure corresponds to the total chlorine input, the chlorine combined in Iron chlorides (two cases : ferric or ferrous chloride production) and the ferric or ferrous chloride produced.

RAW MATERIAL INPUT AND EFFLUENT OUTPUT FOR DIFFERENT ORES
CHLORINE PROCESS

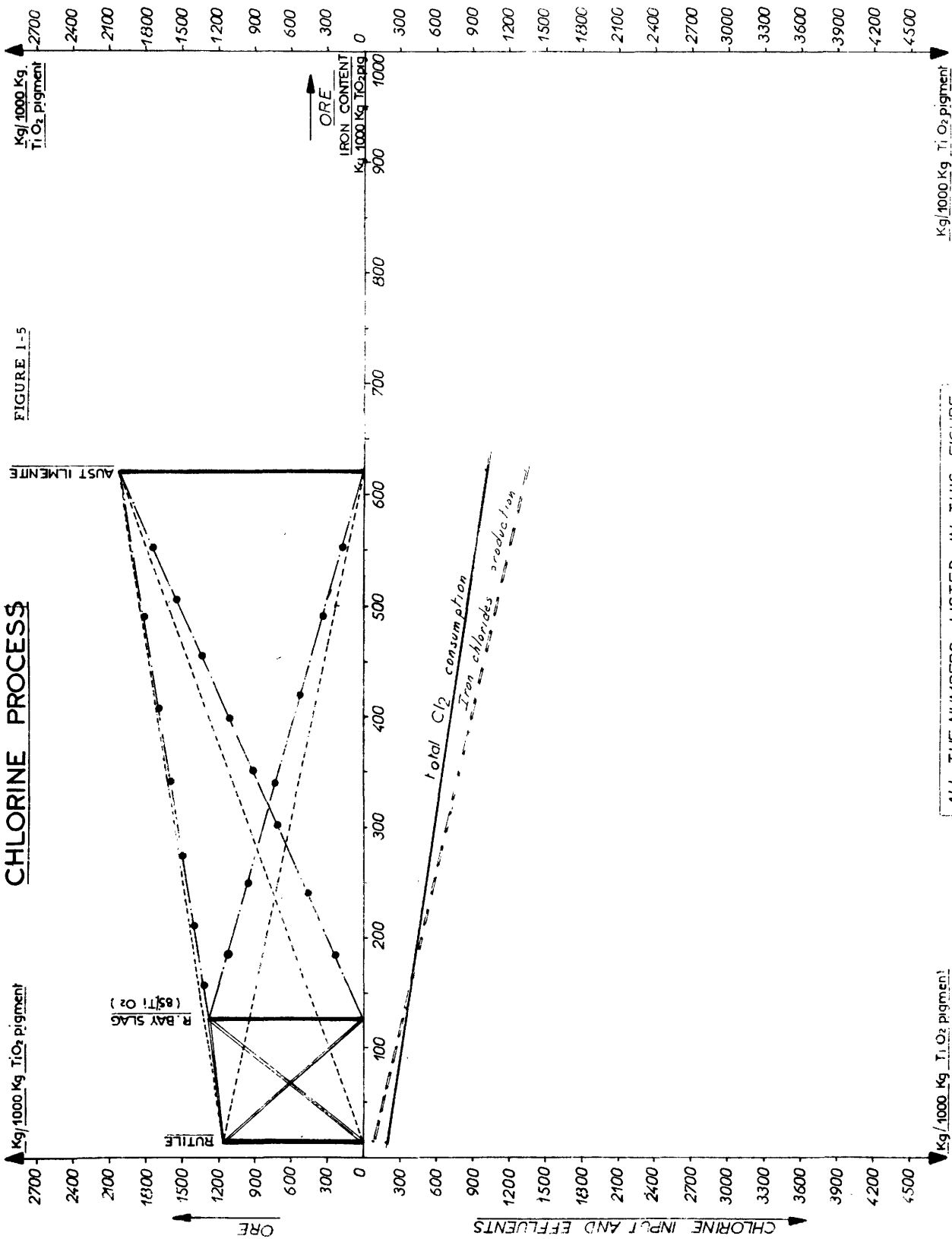


FIGURE 1-5

ALL THE NUMBERS LISTED IN THIS FIGURE ARE REFERRED TO 1 TON OF TiO₂ PRODUCED.

1-2 ECONOMICAL FEATURES

1-2-1 TiO₂ consumption

A- TiO₂ End uses breakdown

We have shown in the table 1-1 :

- the evolution of the TiO₂ end uses breakdown in USA between 1950 and 1974
- the TiO₂ end uses breakdown in USA, W. Germany, G-Britain and Japan during 1968
- the TiO₂ end use breakdown for EEC countries during 1973
- the fraction of TiO₂ pigment as percentage of total white pigments in EEC during 1973
- the fraction of TiO₂ pigment as percentage of total white pigment in USA between 1940 and 1970.

It is not in the present study scope to detail the TiO₂ applications.

In the main consumer countries, the paint, lacquers and printing inks applications represent between 52% and 68% of all the applications.

Paper and plastics are the second and third uses, and represent respectively 6% and 22% of the uses.

The fraction of TiO₂ in the total white pigment is also a good indication to analyze the possible future consumption of a country.

In Europe, UK has the most important fraction of TiO₂ in total white pigment (88%) and France, the least important (54%). The figure for 1973 in UK corresponds to the figures for 1962 in USA whereas the figure for 1973 in France corresponds to the figure for 1952 in USA.

END USE BREAKDOWN FOR TIO₂ IN USA (US BUREAU OF MINES)

	1950 %	1960 %	1970 %	1974 %
Paint and Lacquer	67	56	52	52.6
Paper	9	14	22.4	18.5
Plastics	-	-	6.7	11.3
Floor covering	5	5.6	3.3	1.6
Textiles	2.0	3.0	1.3	1.0
Rubber	3.7	4	2.9	2.7
Other	15.3	21.4	12.7	13.3
TOTAL	100	100	100	100

TIO₂ END-USE BREAKDOWN FOR EEC COUNTRIES %
(1973)

	W. Germany	Benelux	Denmark and Eire	France	Italy	U.K.
Paint and lacquer	65.6	63.6	67.0	59.8	55.	63.
Paper	5.7	7.3	8.0	7.6	10.	6.
Plastics	16.0	10.9	8.0	13.0	12.5	10.5
Textiles	5.0	3.6	-	4.3	6.3	4.5
Rubber	2.5	3.6	-	13.3	3.8	2.3
Other	4.9	11.0	17.0	12.0	12.4	13.7
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0

END-USE BREAKDOWN PER CONSUMER COUNTRIES
1968

	U S A %	W. GERMANY %	G-BRITAIN %	JAPAN %
Paint, lacquers and printing inks	55	68	55	62
Paper	19	7	9	9
Plastics	8	9	10	8
Textiles	1	6	7	6
Rubber	3	6	9	7
Other	14	4	10	8
TOTAL	100	100	100	100

TIO₂ AS PERCENT OF TOTAL WHITE PIGMENTS IN EUROPE
(1973)

	_(weight)
West Germany	87
Benelux	84
France	54
Italie	67
U K	88

TIO₂ AS PERCENT OF TOTAL WHITE PIGMENTS IN U.S.A

	1940 %	1943 %	1950 %	1955 %	1960 %	1965 %	1970 %
USA	25	33	52	71	86	97	97

B- TiO₂ consumption per Capita

We have shown in the table 1-5 the US TiO₂ consumption between 1950 and 1974.

In the same table we have shown the TiO₂ consumption per capita in US and the evolution of the GNP per capita for the same period.

These different figures are plotted and the correlation between the GNP and the TiO₂ consumption per capita can easily be seen between 1950 and 1974 (the correlation coefficient is 0.994).

Following the same analysis we have taken the figures for some other countries in 1973 in order to test a possible correlation per between the TiO₂ consumption per capita and the GNP per capita.

In the table 1-6, the GNP are expressed as percentage of the US GNP.

In the draft the GNP per capita and TiO₂ consumption per capita are expressed as fraction of the US GNP per capita and US TiO₂ consumption per capita.

A certain correlation between GNP per capita can be still seen except for US and UK for which the TiO₂ consumption per capita is very higher than the average value.

C- Future usage

A fine analysis of the total requirement involves an analysis of each TiO₂ end use and the determination of by other materials.

The decline observed in 1974, due to the economic world crisis, and the TiO₂ price increase was temporary.

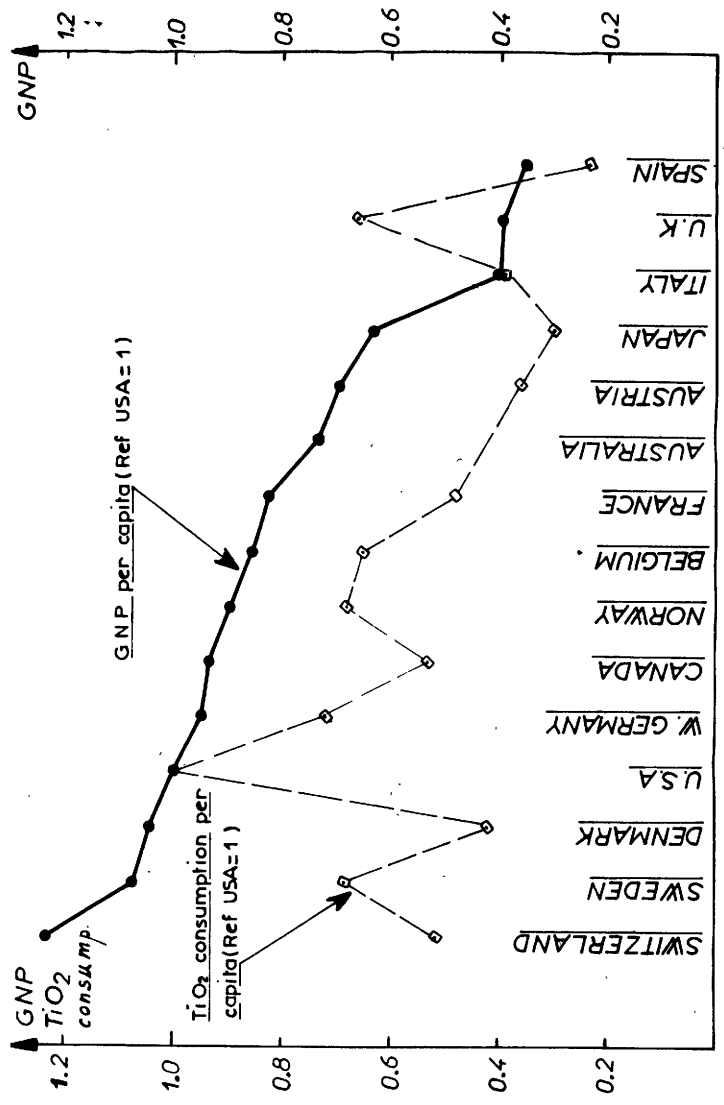
But several years may be needed for on complete recovery.

TiO₂ TOTAL CONSUMPTION AND PER CAPITA CONSUMPTION IN THE EUROPEAN COUNTRIES (1973)

E E C	Total consumption (x 1 000 long tons)	Population MMh	Per capita consumption kg/h
West Germany	160	62.3	2.57
Benelux	55	23.6	2.33
France	90	52.1	1.73
Italy	80	55.44	1.44
U K	133	56.0	2.38
Denmark + Eire	12	8.00	1.50
TOTAL EEC	532	257.44	2.07
Sweden + Norway	30	12.13	2.47
Finland	8	4.7	1.7
Switzerland	12	6.45	1.86
Austria	10	7.55	1.32
Portugal	5	9.9	0.51
Spain	30	35.2	0.85
Greece	5	8.9	0.56
TOTAL (ex EEC)	100	84.83	1.18
TOTAL Europe	632	342.27	1.85

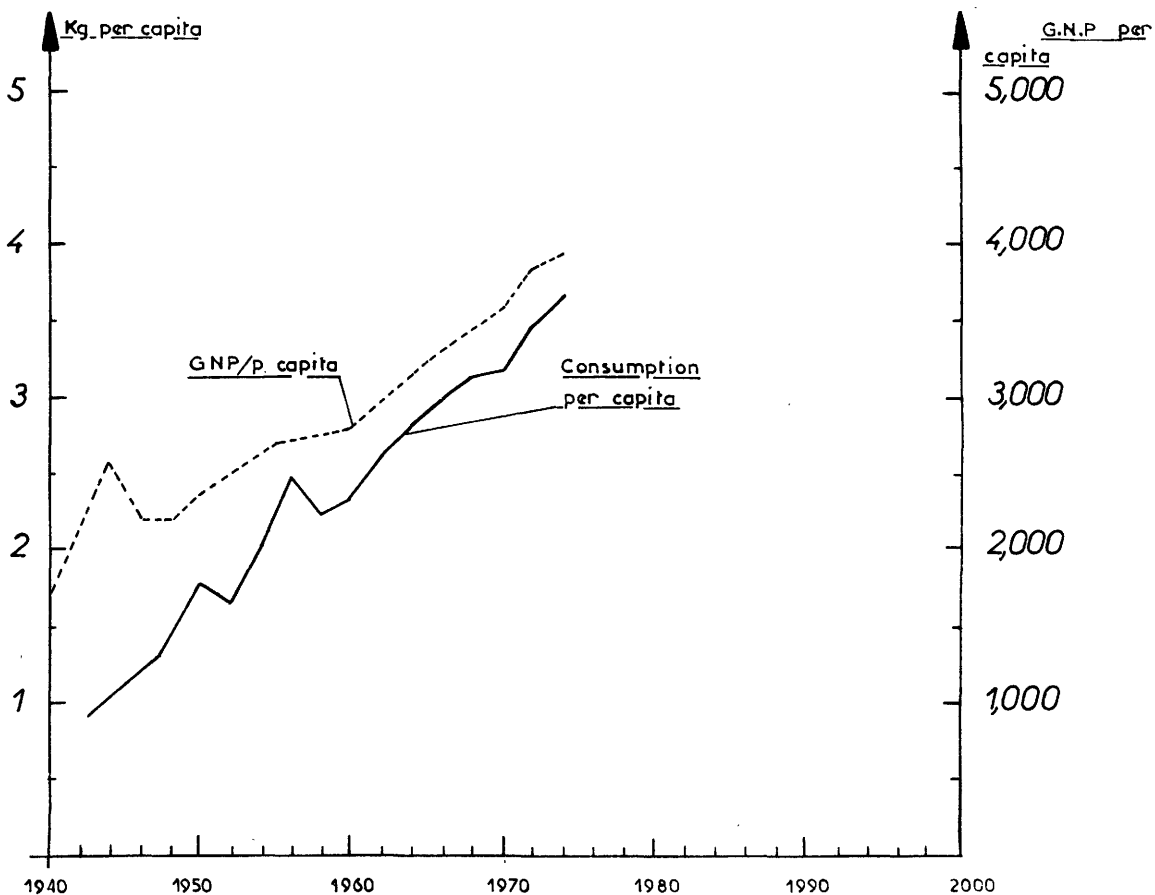
RELATION TiO₂ consumption / GNP

		1974					
Countries	GNP	populat. MM.h	GNP per capit.	Countries	GNP	populat. MM.h	GNP per capit.
Belgium	3.95	9.81	85.4	Argentina	0.58	25.71	4.8
Denmark	2.49	5.07	104.2	Australia	4.63	13.30	73.8
France	21.85	52.54	82.2	Brazil	5.89	104.23	12.0
Italy	10.42	55.44	39.9	Canada	9.89	22.50	93.20
Netherlands	5.12	13.55	80.1	Egypt	0.76	38.00	4.2
U.K.	10.51	56.06	39.7	India	5.82	586.20	2.1
W. Germany	27.92	62.27	95.0	Iran	3.30	32.12	21.8
Austria	2.47	7.55	69.3	Israel	0.54	3.18	36.2
Norway	1.69	3.89	89.7	Japan	32.40	108.60	63.2
Spain	5.88	35.23	35.3	Mexico	4.65	58.2	17.0
Sweden	4.13	8.16	107.3	S. Africa	1.74	22.2	16.7
Switzerland	3.78	6.49	123.4	USSR	38.81	252	28.4
East Ger.	4.16	17.02	51.8	US	100	212	100.0
Poland	4.34	33.81	27.2	Venezuela	1.54	12.3	26.6



TIO₂ CONSUMPTION IN USA

	Global consumption (X1000 metric tons)	US population (MMh)	Consumption per capita. kg/p.capit.	GNP/p. capita constant \$ 1958
1950	271	151.7	1.79	2,342(1950)
1952	251	156.9	1.60	
1954	329	162.4	2.03	2.666(1955)
1956	412	168.2	2.45	
1958	387	174.1	2.22	
1960	430	180.7	2.38	2.699(1960)
1962	481	186.5	2.58	
1964	535	191.8	2.79	
1966	582	196.5	2.96	3.180(1965)
1968	622	200.7	3.10	
1970	638	204.8	3.11	3.528(1970)
1972	749	208.8	3.58	3.795(1972)
1974	765	212.0	3.60	3.873(1974)



Based on the above cited consideration the US Bureau of Mines estimates as possible growth rate of the TiO_2 industry 3%/year in US and 5.2%/year for the rest of World with an average value for the world of 4.5% (1973-2000).

It must be noted that a difference on the growth rate can be considered as a difference in the objectif for a given period or a difference of period for a given objectif.

E.g. A growth rate of 4% instead of 5% means that an objectif is reached in 15 years instead of 12 years. This last aspect will be kept in mind in the present study.

1-2-2 TiO₂ price (Ref : E C N)

We have shown in the table 1-7 and figure 1-6 the evolution of the TiO₂ prices between July 1974 and February 1977 in USA, Belgium, France, Germany, UK, Italy.

These prices are converted into US dollars taking into account the exchange rate in the corresponding period.

At present, the highest prices are in the USA, with a difference of 3% in the case of Italy and 23% in the case of the UK.

The increase in the US prices between July 74 and Feb 77 was about 90% whereas it was about 30% in the case of the Italian prices.

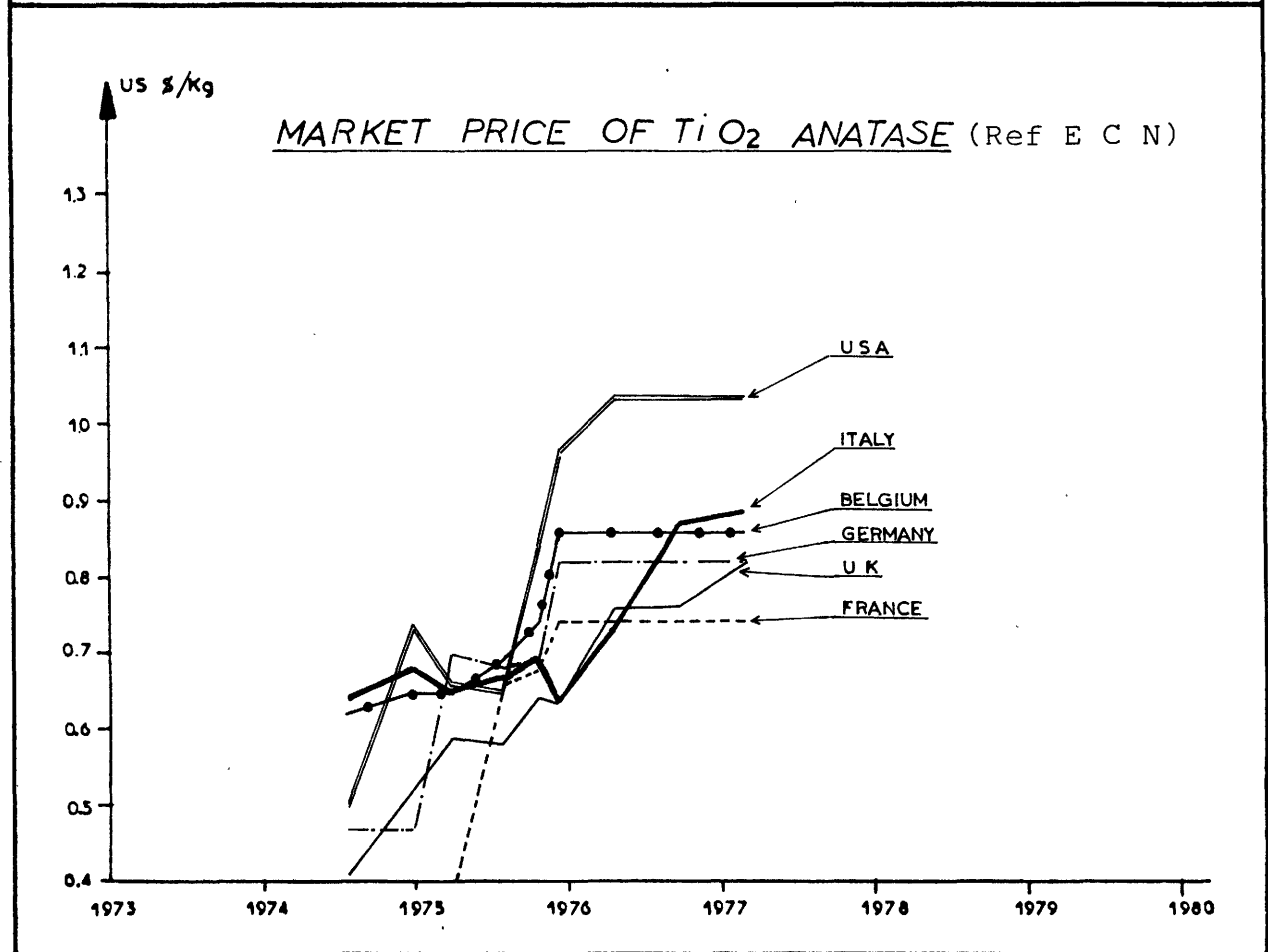
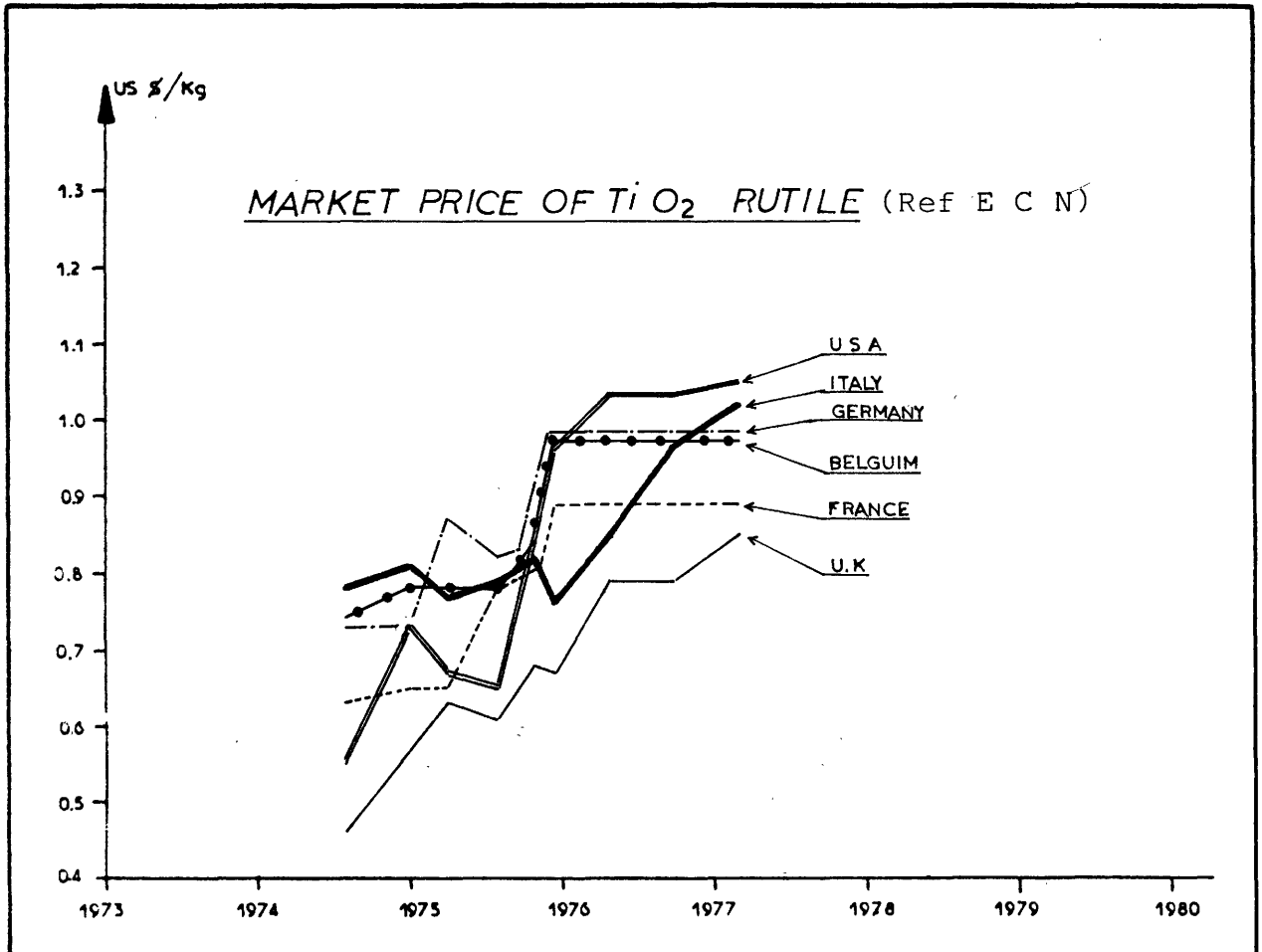
This increase of 30% corresponds to the increase in the cost of production during this period.

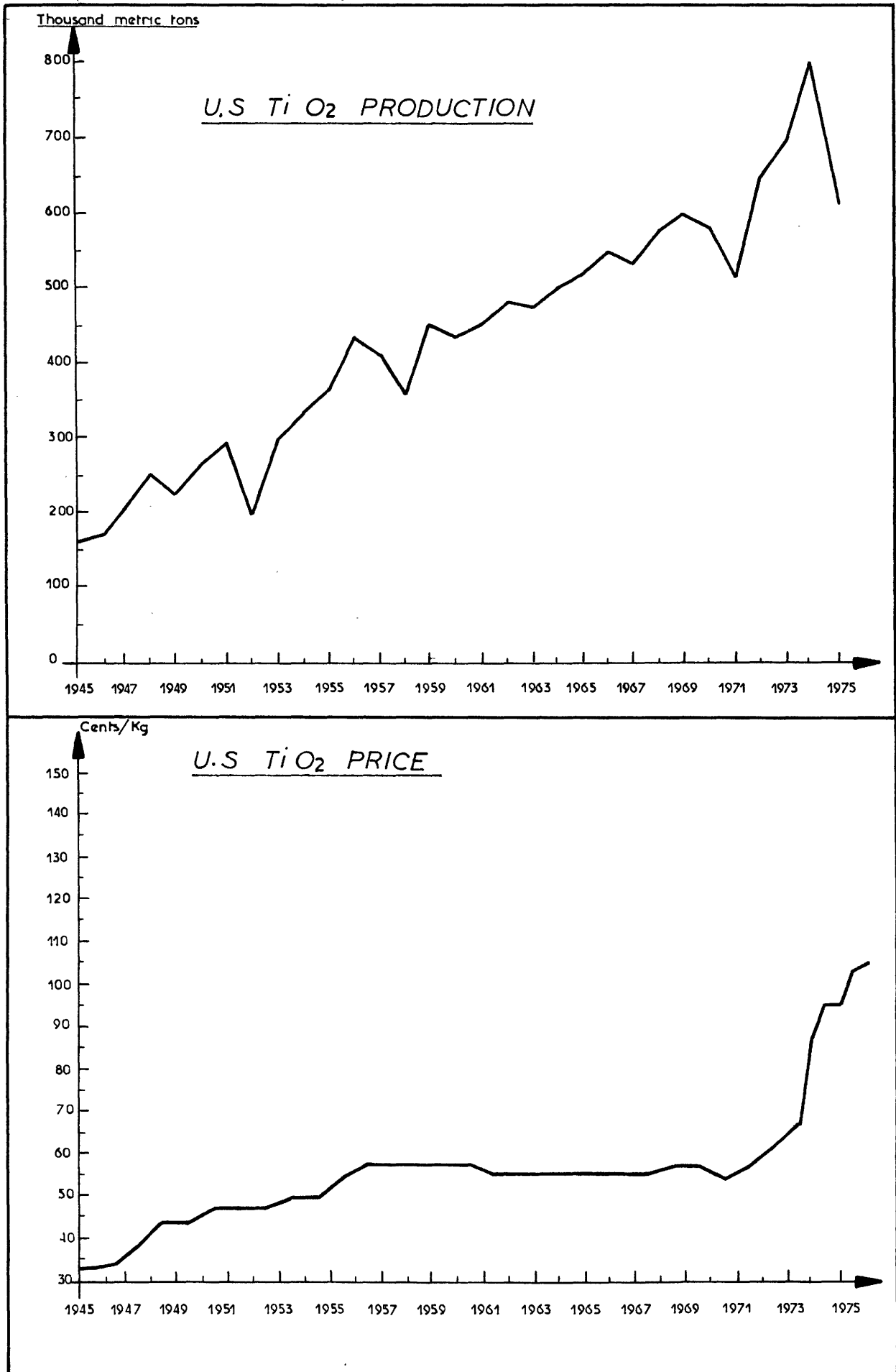
MARKET PRICE OF TiO ₂ RUTILE US \$/Kg						
Price without taxes	U.S.A.	Belgium	France	Germany	Italy	U.K.
July 1974	0.55	0.74	0.63	0.73	0.78	0.46
January 1975	0.73	0.78	0.65	0.73	0.81	-
March 1975	0.67	0.78	0.65	0.87	0.77	0.63
July 1975	0.65	0.78	0.79	0.82	0.79	0.61
October 1975	0.84	0.84	0.81	0.83	0.82	0.68
November 1975	0.96	0.97	0.89	0.98	0.76	0.67
April 1976	1.03	0.97	0.89	0.98	0.85	0.79
September 1976	1.03	0.97	0.89	0.98	0.97	0.79
February 1977	1.05	0.97	0.89	0.98	1.02	0.85

Increase

July 1974- Feb. 1977	90%	31%	41%	34%	30%	84%
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MARKET PRICE OF TiO ₂ ANATASE US \$/kg						
Price without taxes	U.S.A.	Belgium	France	Germany	Italy	U.K.
July 1974	0.50	0.62	0.36	0.47	0.64	0.41
January 1975	0.73	0.65	0.37	0.47	0.68	-
March 1975	0.66	0.65	0.37	0.70	0.65	0.59
July 1975	0.65	0.69	0.66	0.68	0.67	0.58
October 1975	0.84	0.74	0.68	0.69	0.69	0.64
November 1975	0.96	0.86	0.74	0.82	0.64	0.63
April 1976	1.03	0.86	0.74	0.82	0.73	0.76
September 1976	1.03	0.86	0.74	0.82	0.87	0.76
February 1977	1.03	0.86	0.74	0.82	0.89	0.82





1-2-3 TiO₂ trade

It is not within the scope of this study to analyse the TiO₂ trade, we have just given some statistics in order to show main exporting and importing countries and also, the important cross trading between TiO₂ producing countries .

Moreover, it must be noted that even when there is an important production, the links between producers and customers are very close. For this reason it is very difficult for a new producer to develop, sales in a country : e.g. although countries such as India and Malaysia appear to be

in a good position to produce TiO₂ pigment, their own production of TiO₂ is restricted by the difficulty of exporting their output to the main consuming countries such as Japan, U.S.A. et EEC.

U.S. IMPORTS AND EXPORTS OF TITANIUM DIOXIDE
(thousand tonnes)

	<u>Imports</u>	<u>Exports</u>	<u>Net imports</u>
1968	48.5	13.7	34.8
1969	48.4	12.7	35.7
1970	54.8	16.4	38.4
1971	38.9	12.7	26.2
1972	78.4	9.0	69.4
1973	55.0	18.8	36.2

SECTION 2

EXAMINATION OF THE ECONOMICS OF THE PROCESSES

SECTION 2

EXAMINATION OF THE ECONOMICS OF THE PROCESSES

2-1 Introduction

2-2 Upgrading processes

2-3 Pigment production

2-4 Treatment processes

2-5 Raw material economics

2-1 INTRODUCTION

In this chapter we have done the basic economic calculations allowing to compare the total cost of the different routes described in the general figure "OVERALL TECHNICAL PATTERN OF TiO₂ INDUSTRY".

SUMMARY OF THE MAIN ECONOMIC DATA

END 1976

Prices are expressed in U.C.

SYNTHETIC RUTILE PROCESSES

	Prod: 100,000/y	BENILITE (Loc Aust)	BENILITE C (Loc Aust)	WEST. TITANIUM (Loc Aust)	ISHIHARA S K (Loc Aust)	MURPHORES (Loc Aust)
Total INVESTMENT	32 MUC/100,000t/y	24 MUC/100,000t/y	22 MUC/100,000t/y	22 MUC/100,000t/y	22 MUC/100,000t/y	32 MUC/100,000t/y
R. Material UC/t	35.3	35.3	29.4%	45.2	109.2 (with treat)	47.7
Utilities Cost UC/t	42.2	42.2	35.2%	12.5	28.0	37.3
Operating Cost UC/t	17.6	9.1	7.6%	16.3	12.5	19.0
Overhead Cost UC/t	50.1	33.4	27.8%	37.3	34.9	51.4
Cost of Production	145.2	120.0	100%	111.3	184.7	155.4
Transfer price UC/t	209.2 UC/t	168 UC/t	S. Rutile	155.3 UC/t	228.7 UC/t	219.4 UC/t
						S. Rut.

-(Return 20%)

TiO₂ PIGMENT PROCESSES

	Prod: 33,000/y TiO ₂	R.M Rutile	R.M A Bay S	R.M. Lowgrade	Sulfur pr.	R.M. Rut. Im
Total INVESTMENT	50 MUC/33,000t/y TiO ₂	57.5 MUC/33,000t/y Ti	64 MUC/33,000t/y Ti	46 MUC/33,000t/y Ti		
R. Material UC/t	1.17Y+0.35A+0.21 B	1.3Y +0.36A+0.5B	1.8Y+0.47A+2.5B	2X+1.15C+45.3		
Utilities Cost UC/t	43.7	50.9	71.8	101.6		
Operating Cost UC/t	140.4	157.1	170.9	157.3		
Overhead Cost UC/t	275.8	313.1	344.7	254.5		
Cost of Production	459.6 + R Mater.	521 + R. Mater	597.2 + R Mater.	513.4 + R. Mater		
Transfer price UC/t	687 + R Mater.	782.4 + R. Mater	878.4 + R. Mater	722.5 + R. Mater		

TREATMENT AND REGENERATION PROCESSES

	Cl ₂ regen: KEL-CHLOR	Chlorides Hydrolysis	Sulfuric acid conc.	Treatment I
Total INVESTMENT	4.15 MUC/25,000t/y Cl ₂	3.3 MUC/31,000	4.4 MUC/33,000t/y	10.4 MUC/33,000t/y
R. Material UC/t	7.6	by product	Effluents	Credit(s) 39.
Utilities Cost UC/t	2.2	25.5	14.1	64.5
Operating Cost UC/t	16.8	11.2	5.2	28.2
Overhead Cost UC/t	31.6	26.2	8.9	56.5
Cost of Production	58.2	62.9	28.2	157.2
Transfer price UC/t	83.1 UC/t	78.9 UC/t	34.4 UC/t	204.5
	Cl ₂	HCl 100%	62% wt	TiO ₂

- (1) based on Woodall Duckham process
- (2) Vacuum concentration (double effect)
- (3) Concentration-roasting - neutral.
- (4) Concentration-roasting - neutral. (Return 15%)

2-2 UPGRADING PROCESSES

2-2-1 Introduction

In this chapter we have calculated the synthetic rutile cost of production made by the main processes presently available.

e.g. Benilite Corp
Western Titanium
Ishihara S.K.
Murphyores

These calculations were not carried out for the sake of comparing the economics but to determine the possible S. Rutile price range. As a matter of fact, a comparative analysis would have required a fine analysis of each specific context in which each process can be located.

We have considered two typical locations :

- . Australia
- . India

For each of these locations we have adjusted the capital and labor costs to the local conditions. But all the other figures, notably the utilities costs have been kept equal.

The local incidence on the capital and labor cost have been determined by talking with local companies. It must be noted that the incidence on the capital cost can greatly vary even in the same country. The time of realization, the number of imported equipments can modify the total capital cost.

The bases of the calculations are as follows :

- Ilmenite price : 15 UC/t

This price is an average sales price but without freight cost, but if a plant is built far from mineral sources it would be necessary to add a freight cost on the ilmenite

and to modify the freight cost of S. Rutile.

We have considered the same price for all the processes but it must be noted that a process such as the Murphoyes process can use high chromium content and is consequently cheaper.

- HCl price

The HCl price can vary considerably with the local context. In some locations (e.g. India) the market in such (sales to the Gulf) that the HCl by product can be sold. We have considered a price of 45 UC/t (35%) as a typical price of such a situation.

In any case it must be noted that for economic or environmental reasons the upgrading plant regenerates HCl acid and therefore uses only few HCl. This fact limits the consequence of HCl price on the S. Rutile cost of production.

- Other raw material

A part from the hydrogen price, the other raw material prices are based on local information.

- Utilities cost

Except for the Western Titanium process, the main factor of the utilities cost is the fuel price and this very fuel price is relatively constant in the various countries and is presently about 68 UC/t. Nevertheless, considering local indications we have taken for the Australian location a fuel price of 58 UC/t. In any case we can note that for the processes having a high fuel consumption a variation of the fuel price from 58 UC/t to 70 UC/t lead to an increase of the synthetic rutile price of 6.7 UC/t.

In some location, electricity can be available at a very low price, a price of 15 UC/1000 Kwh (US) instead of 27 UC/1 000 Kwh (Australia).

This cost differential reduces the S. Rutile price by about 4.2 UC/t.

- Operating costs (from local information) :

. Australian location :

labor : 12,000 UC/y
supervision : 18,000 UC/y

. Indian location

labor : 3,000 UC/y
supervision : 5,400 UC/y

- Maintenance

7% of total investment including labor and material

- Overhead expenses

We have taken typical figures

- . Direct overhead 30%/Lab. cost
- . Gen. Plant overhead 65%/Op cost
- . Insurance, taxes 15% Total Invest.
- . Depreciation 10% Total Invest.

- By-product credit

Ferric oxide : No credit

- Return on investment:20% total investment

A- Benilite process

The economic calculations are based on published information from Benilite Corp of America.

The fuel consumption includes the HCl regeneration step based on the Woodall Duckham process.

No value has been claimed for the ferric oxide obtained as by-product.

The total investment, 32 MUC (1976) for a 100,000 t/y TiO_2 plant corresponds to a US Gulf site. The same investment has been taken for an Australian site. A 22 MUC investment has been mentioned to us for an Indian or Malaysian location, but 24 MUC seems to us to be a more updated figure.

<u>COST OF PRODUCTION</u>					DATE: End 1976	
<u>PRODUCT</u> SYNTHETIC RUTILE			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u> BENILITE CORP			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u> AUSTRALIA			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> 100 000 t/y			<u>TOTAL</u>		32 MUC	
<u>ON STREAM TIME</u> 8 000 h						
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/year (mUC)	Cost/unit (uc)	
Ilmenite	190,000	t	15	2,850		
HCl (31,5%)	15,000	t	45	675		
<u>TOTAL RAW MATERIALS COST</u>				3,525	35.25	
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit			
Electricity	35,000	1000kwh	27	945		
Cooling Water	1,200	1000m ³	20	24		
Bl. Water		1000m ³				
Proc. Water		1000m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	56,000	l.ton	58	3,248		
<u>TOTAL UTILITIES COST</u>				4,217	42.17	
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)				
Labor	48	12,000		576		
Supervision	3	18,000		54		
Maintenance (Material and labor)	%Tot. Inv.			1,128		
<u>TOTAL OPERATING COSTS</u>				1,758	17.58	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30% LABO. COST			189		
General Plant overhead	65% OP. COST			1,142		
Insurance, Taxes	1.5% TI			480		
Depreciation	10% TI			3,200		
<u>TOTAL OVERHEAD EXPENSES</u>				5,011	50.11	
<u>COST OF PRODUCTION</u>				14,511	145.11	
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit			
Fe ₂ O ₃		t	0	0		
<u>TOTAL BY PRODUCT CREDIT</u>				0		
<u>NET COST OF PRODUCTION</u>				14,511	145.11	
<u>RETURN ON INVESTMENT 20% TI</u>				6,400	64.00	
<u>SALES EXPENSES</u>				very low		
<u>TRANSFER PRICE</u>				20,911	209.11	

<u>COST OF PRODUCTION</u>					DATE: End 1976	
<u>PRODUCT</u> SYNTHETIC RUTILE			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u> BENILITE CORP			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u> INDIA			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> 100 000 t/y			<u>TOTAL</u> 24 MUC			
<u>ON STREAM TIME</u> 8 000 h						
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/year(mUC)	Cost/unit (uc)	
Ilmenite	190,000	t	15	2,850.		
HCl (31,5%)	15,000	t	45	675.		
<u>TOTAL RAW MATERIALS COST</u>				3,525	35.25	
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit			
Electricity	35,000	1000kwh	27	945		
Cooling Water	1,200	1000m ³	20	24		
Bl. Water		1000 m ³				
Proc. Water		1000 m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	56,000	l.ton	58	3,248		
<u>TOTAL UTILITIES COST</u>				4,217	42.17	
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)				
Labor	48	1200		57.6		
Supervision	3	2200		6.6		
Maintenance (Material and labor) % ISBL inv.				846		
<u>TOTAL OPERATING COSTS</u>				910.2	9.10	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30% LABO. COST			19.26		
General Plant overhead	65% OP. COST			591.26		
Insurance, Taxes	1.5% TI			360		
Depreciation	10% TI			2,400		
<u>TOTAL OVERHEAD EXPENSES</u>				3,370.5		
<u>COST OF PRODUCTION</u>				12,022,7	120.2	
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit			
Fe ₂ O ₃		t	0	0		
<u>TOTAL BY PRODUCT CREDIT</u>						
<u>NET COST OF PRODUCTION</u>				12,022,7	120.2	
RETURN ON INVESTMENT 20% TI				4,800		
<u>SALES EXPENSES</u>						
<u>TRANSFER PRICE</u>				16,822,7	168.2	

B- Western Titanium process

The cost calculations are based on information given by the Western Titanium company.

The main consumptions are for ilmenite from Capel as raw material.

The use of Ilmenite from Capel instead of ilmenite from Eneabba (higher TiO_2 content) can cut the cost of production by about 15%.

The by products value has been taken at zero. The cost of neutralizing the leaching solution is included in the investment cost and in the Raw material cost.

A total investment of 22 MUC (1976) has been mentioned for an Australian location.

<u>COST OF PRODUCTION</u>					DATE: End 1976	
<u>PRODUCT</u> SYNTHETIC RUTILE			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u> WESTERN TITANIUM			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u> AUSTRALIA			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> 100 000 t/y			<u>TOTAL</u> 22 M UC			
<u>ON STREAM TIME</u> 8 000h						
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/year(muc)	Cost/unit (uc)	
Ilmenite	190,000	t	15	2,850		
Coal	80,000	t	12	960		
Ferrous sulfate	18,000	t				
Am chloride	1,200	t	254	304.8		
Limestone	8,000	t	8.49	67.92		
Sulfuric acid	6,000	t	56	336		
<u>TOTAL RAW MATERIALS COST</u>				4,518.720	45.1872	
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit			
Electricity	29,000	1000kwh	27	783		
Cooling Water	1,600	1000m ³	20	32		
Bl. Water		1000m ³				
Proc. Water		1000m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	7,500	l.ton	58	435		
<u>TOTAL UTILITIES COST</u>				1,250	12.5	
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)				
Labor				332		
Supervision				137		
Maintenance (Material and labor)				1,157		
<u>TOTAL OPERATING COSTS</u>				1,626	16.26	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30% LABO. COST			140.7		
General Plant overhead	65% OP. COST			1,056.9		
Insurance, Taxes	1.5% TI			330		
Depreciation	10% TI			2,200		
<u>TOTAL OVERHEAD EXPENSES</u>				3,727.6		
<u>COST OF PRODUCTION</u>				11,122.32	111.2	
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit			
<u>TOTAL BY PRODUCT CREDIT</u>						
<u>NET COST OF PRODUCTION</u>				11,122.32	111.2	
RETURN ON INVESTMENT 20% TI				4,400	44	
SALES EXPENSES				very low		
<u>TRANSFER PRICE</u>				15,522.32	155.2	

C- Ishihara S.K. Process

There are no precise figures available for the total investment cost. If we consider the equipment required for this process and compare this with that needed for the other processes, a total investment of 22 MUC to us reasonable.

It must be carefully noted that we have included a cost of treatment for the copperas by-product.

This means that, on this assumption, the cost of production by the ISK process does not take into account the special advantages of the Yokaichi works.

<u>COST OF PRODUCTION</u>					DATE: End 1976	
<u>PRODUCT</u> SYNTHETIC RUTILE			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u> ISHIHARA SANGYO K			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> 100.000t/yr			<u>TOTAL</u> 22 MUC			
<u>ON STREAM TIME</u> 8 000h						
<u>RAW MATERIALS</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price</u> uc/unit	<u>Cost/year(muc)</u>	<u>Cost/unit (uc)</u>	
Ilmenite	190,000	t	15	2,850		
Coke	9,500	t	50	475		
Sulfuric acid	treatment of copperas					
	included					
	190,000	t	40	7,600		
<u>TOTAL RAW MATERIALS COST</u>				10,925	109.2	
<u>UTILITIES</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price</u> uc/unit			
Electricity	30,000	1000kwh	27	810		
Cooling Water	1,200	1000m ³	20	24		
Bl. Water		1000m ³				
Proc. Water		1000m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	33,900	l.ton	58	1,966.2		
<u>TOTAL UTILITIES COST</u>				2,800.2	28	
<u>OPERATING COSTS</u>	<u>Total men</u>	<u>Cost/year(uc)</u>				
Labor	36	12,000		432		
Supervision	3	18,000		54		
Maintenance (Material and labor) 7% TI				770		
<u>TOTAL OPERATING COSTS</u>				1,256	12.5	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30% LABO COST			145.8		
General Plant overhead	65% OP. COST			816.4		
Insurance, Taxes	1.5% TI			330		
Depreciation	10% TI			2,200		
<u>TOTAL OVERHEAD EXPENSES</u>				3,492.2	34.9	
<u>COST OF PRODUCTION</u>				18,473.4	184.7	
<u>BY PRODUCT CREDIT</u>	<u>Quantit</u>	<u>Unit</u>	<u>PRICE</u> uc/unit			
Fe ₂ O ₃	0					
<u>TOTAL BY PRODUCT CREDIT</u>				0		
<u>NET COST OF PRODUCTION</u>				18,473.4	184.7	
RETURN ON INVESTMENT 20% TI				4,400		
<u>SALES EXPENSES</u>						
<u>TRANSFER PRICE</u>				22,873.4	228.7	

D- Murphyores process

The main utilities and raw material consumptions and the labour requirements have been given by the Murphyores company.

It must be noted that we have assumed an ilmenite price of 15 UC/t ; this price is lower if an high chromium content ilmenite is used as raw materials. E.g. if the ilmenite cost is 7.5 UC/t instead of 15 UC/t, then the cost of production decreases by about 15 UC/t. The fuel consumption includes the HCl regeneration step e.g. that based on the Lurgi process.

No information is available on the total investment. This has been evaluated as equal to the cost of a Benilite process plant.

The investment for the production of hydrogen is included in the hydrogen price which is used in the cost calculation.

<u>COST OF PRODUCTION</u>				DATE: End 1976	
<u>PRODUCT</u> SYNTHETIC RUTILE			<u>CAPITAL INVESTMENT</u>		
<u>PROCESS</u> MURPHYORES			<u>INSIDE BATT. LIMITS</u>		
<u>LOCATION</u> AUSTRALIA			<u>OUTSIDE BATT. LIMITS</u>		
<u>CAPACITY</u> 100,000 t/y			<u>TOTAL</u> 32 MUC (no precise in- form.available)		
<u>ON STREAM TIME</u> 8 000h					
<u>RAW MATERIALS</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>	<u>Cost/year(muc)</u>	<u>Cost/unit (uc)</u>
Ilmenite (55%)	183,000	t	15**	2,745	
HCl (31,5%)	5,000	t	45	225	
Hydrogen	15,000	1000m ³	120	1,800	
<u>TOTAL RAW MATERIALS COST</u>				4,770	47.7
<u>UTILITIES</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>		
Electricity	30,000	1000kwh	27	810	
Cooling Water	800	1000m ³	20	16	
Bl. Water		1000 m ³			
Proc. Water		1000 m ³			
Steam H. P.		l. ton			
Steam L. P.		l. ton			
Fuel	50,000	l. ton	58	2,900	
<u>TOTAL UTILITIES COST</u>				3,726	37.26
<u>OPERATING COSTS</u>	<u>Total men</u>	<u>Cost/year(uc)</u>			
Labor	60	12,000	720		
Supervision	3	18,000	54		
Maintenance (Material and labor)				1,128	
<u>TOTAL OPERATING COSTS</u>				1,902	19.02
<u>OVERHEAD EXPENSES</u>					
Direct Overhead	30% LABO. COST		232.2		
General Plant overhead	65% OP. COST		1,236		
Insurance, Taxes	1.5% TI		480		
Depreciation	10% TI		3,200		
<u>TOTAL OVERHEAD EXPENSES</u>				5,148.2	51.4
<u>COST OF PRODUCTION</u>				15,546.2	155.4
<u>BY PRODUCT CREDIT</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>		
<u>TOTAL BY PRODUCT CREDIT</u>					
<u>NET COST OF PRODUCTION</u>				15,546.2	155.4
RETURN ON INVESTMENT 20% TI				6.400	64
<u>SALES EXPENSES</u>					
<u>TRANSFER PRICE</u>				21,946.2	219.4

** : It should be noted that this process can be fed with ilmenite with an high chromium content.

2-3 PIGMENT PRODUCTION

In this chapter we have estimated the net cost of TiO_2 production via :

- sulfate process (with Ilmenite as raw material)
- chlorine process (with
 - . Rutile
 - . Rich. Bay Slag (hyp.)
 - . Ilmenite as raw materials)

These calculations have been done on the following basis for the two processes :

- European location
- Utilities cost
 - . Electricity 28 UC/1 000 Kwh
 - . C. Water 20 UC/1 000 m3
 - . P. Water 360 UC/1 000 m3
 - . Fuel 70 UC/t
- Labor cost
 - . Labor 14,000 UC/y
 - . Supervision 18,000 UC/y
- Return on investment : 15%

We will detail the assumptions taken into account in the cost calculations before each calculation.

2-3-1 Sulfate route

A- Sulfate route using ilmenite

Ilmenite and sulfur prices

The ilmenite and the sulfur prices have been considered as parameters (X and C) in the economic calculations. These parameters will be examined in the chapter 2.5 of this section.

Raw material consumption

The raw material consumption correspond to Australian ilmenite.

Utilities consumption

Fuel consumption includes steam production.

Depreciation

The depreciation rate has been taken at 8%, which corresponds to an amortization of 12 years.

Return on investment

This has been taken at 15% for all the TiO_2 pigment processes.

Investment

The investment is based on published information. These investments are converted to present value by using the CE cost index.

Therefore the investment cost is 1,400 UC per tonne of TiO_2 produced per year.

B- Sulfate route using slag

We have considered two sources of slag

- Canadian slag (70% TiO_2)
- Richard Bay Slag (85% TiO_2)

In a first cost calculation, we have taken into account only the new raw material consumptions which are required when slag mineral is used instead of ilmenite mineral.

It may be noted that if the capital cost were to increase by 10%, the transfer price would increase by 5%.

On the assumption that the capital cost is 10% lower when slag mineral is used instead of ilmenite mineral ; it is quite reasonable to think that at the same TiO_2 transfer price, slag as raw material can be 20 UC/t higher.

For the sulfate process with Canadian slag as raw material
Raw material consumptions are assumed as follow :

- 1,6t Canadian slag/1t TiO_2 pigment
- 2,8t H_2SO_4 /1t TiO_2 pigment
- no scrap Iron

For the sulfate process with Richard Bay slag as raw material
Raw material consumptions are assumed as follow

- 1,4t R.Bay slag/1t TiO_2 pigment
- About 2.2t H_2SO_4 /1t TiO_2 pigment
- no Scrap Iron

COST OF PRODUCTION					DATE: End 1976
<u>PRODUCT</u> TiO ₂ pigment			<u>CAPITAL INVESTMENT</u>		
<u>PROCESS</u> SULFATE			<u>INSIDE BATT. LIMITS</u>		
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>		
<u>CAPACITY</u> 33,000 t/y(TiO ₂)			<u>TOTAL</u> 46 MUC **		
<u>ON STREAM TIME</u> 8 000h					
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/year(mUC)	Cost/unit (uc)
Ilmenite	66,000	t	X	66X	
Sulfur	37,714	t	C	37.714 C	
Caustic Soda (50%)	3,300	t	50	165	
Scrap Iron	6,600	t	30	198	
Misc.	4,540	t	250	1135	
<u>TOTAL RAW MATERIALS COST</u> 1498 + 66 X + 37.71 C					
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit		
Electricity	34,320	1000kwh	28	960.96	
Cooling Water	6,666	1000m ³	20	133.32	
Bl. Water		1000m ³			
Proc. Water	1,732	1000m ³	360	622	
Steam H. P.		l.ton			
Steam L. P.		l.ton			
Fuel	23,364	l.ton	70	1,635.48	
<u>TOTAL UTILITIES COST</u>				3,351.76	101.57
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)			
Labor	130	14,000		1,820.00	
Supervision	20	18,000		360.00	
Maintenance (Material and labor)	7% T.I			3,010	
<u>TOTAL OPERATING COSTS</u>				5,190	157.27
<u>OVERHEAD EXPENSES</u>					
Direct Overhead	30% LABO. COST			654	
General Plant overhead	65% OP. COST			3,373.5	
Insurance, Taxes	1.5% TI			690	
Depreciation	8% T.I			3,680	
<u>TOTAL OVERHEAD EXPENSES</u>				8,397.5	254.47
<u>COST OF PRODUCTION</u> 18,437.26 + 66X + 37.71C					513.3+RM
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit		
<u>TOTAL BY PRODUCT CREDIT</u>					
<u>NET COST OF PRODUCTION</u> 18,437.26 + 66X+37.71C					513.3+R.M.
RETURN ON INVESTMENT	15%T.I.			6,900	
<u>SALES EXPENSES</u>					
<u>TRANSFER PRICE</u> 25,337.26 + 66X + 37.71 C					

** Sulfuric acid production included

2-3-2 Chlorine routeA- Chlorine route using RutileRaw material costs

The prices of rutile, coke and chlorine have been taken as parameters (respectively Y, A, B)

The oxygen cost has been taken into account in the total investment and utilities consumption.

Raw material and utilities consumptions have been detailed on the economic calculation sheet.

Depreciation

In this case the depreciation rate is 10% which corresponds to amortization over ten years.

Return on investment

We have taken the same value as that for the sulfate process i.e. 15% total investment.

Investment

Some published figures for chlorine process unit have been converted to present values, and so the capital cost for a natural rutile feed, including the oxygen production is 1520 UC per TiO_2 per year.

B- Chlorine route using Richard Bay Slag

It is doubtful whether such slag would be used but we have calculated the TiO_2 transfert price for this route to evaluate the possible economic advantage of this route.

Raw material consumption

The chlorine consumption has been increased to take into account the chlorination of the iron content of this raw material.

Mineral consumption is based on its TiO_2 content with the same yield as for the natural rutile.

Utilities consumption

The oxygen consumption remains the same while the iron content is higher.

Let R be the ratio between the number of moles which react in the chlorination step with R. Bay slag as raw material and the number of moles which react in the chlorination step with rutile as raw material. The new utility consumptions have been established by keeping 1/3 of the remaining utility consumption constant and then by multiplying 1/3 of the remaining utility consumption by R.

Labor requirement

We have assumed additional two men per shift for the chlorination step.

Investment

The total investment can be estimated approximately using the following formula, where I_1 is the total investment for a rutile feed, and I_2 the total investment for a slag feed.

$$I_2 = R^{0.8} \times \frac{2}{3} \times I_1 + \frac{1}{3} I_1 = \frac{I_1}{3} \left[1 + 2 R^{0.8} \right]$$

Such a calculation is purely hypothetical

COST OF PRODUCTION						DATE: End 76	
<u>PRODUCT</u> TiO ₂ pigment			<u>CAPITAL INVESTMENT</u>				
<u>PROCESS</u> CHLORINE (R. Bay Slag)			<u>INSIDE BATT. LIMITS</u>				
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>				
<u>CAPACITY</u> 33,000 t/y			<u>TOTAL</u> 57.5 MUC				
<u>ON STREAM TIME</u> 8,000h							
RAW MATERIALS	Quantit	Unit	Price uc/unit	Cost/year(muc)	Cost/unit (uc)		
Slag 85%	42,900	t	Y	42,9 Y			
Coke	11,800	t	A	11,8 A			
Chlorine	16,500	t	B	16,5 B			
Oxygen	Included in Utilities and Invest						
TOTAL RAW MATERIALS COST 42,9Y+11,8A + 16,5B							
UTILITIES	Quantit	Unit	Price uc/unit				
Electricity	29,205	1000kwh	28	817.74			
Cooling Water	3,388	1000m ³	20	67.76			
Bl. Water		1000 m ³					
Proc. Water		1000 m ³					
Refrig	4,752	ton	24	114.05			
Steam L. P.		l.ton					
Fuel	9,735	l.ton	70	681.45			
TOTAL UTILITIES COST				1.681,00	50,94		
OPERATING COSTS	Total men	Cost/year(uc)					
Labor	70	14,000		980			
Supervision	10	18,000		180			
Maintenance (Material and labor) 7%			TI	4,025			
TOTAL OPERATING COSTS				5,185	157.12		
OVERHEAD EXPENSES							
Direct Overhead	30% LABO COST			348			
General Plant overhead	65% OP. COST			3,370.25			
Insurance, Taxes	1.5% TI			862.5			
Depreciation	10% TI			5,750			
TOTAL OVERHEAD EXPENSES				10,330.75	313.05		
COST OF PRODUCTION 17,196 + 42.9 Y + 11,8A + 16,5B							
BY PRODUCT CREDIT	Quantit	Unit	Price uc/unit				
TOTAL BY PRODUCT CREDIT							
NET COST OF PRODUCTION 17,196 + 42.9Y + 11.8A + 16.5B							
RETURN ON INVESTMENT 15% TI				8,625			
SALES EXPENSES							
TRANSFER PRICE 25,821.7 + 42.9Y+ 11.8A + 16,5B							

COST OF PRODUCTION					DATE End 76	
<u>PRODUCT</u> TiO ₂ pigment			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u> CHLORINE (rutile)			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> 33,000 t/y(TiO ₂)			<u>TOTAL</u> 50 MUC			
<u>ON STREAM TIME</u> 8 000h						
RAW MATERIALS	Quantit	Unit	Price uc/unit	Cost/year(muc)	Cost/unit (uc)	
Rutile	38,610	t	Y	38.61 Y		
Coke	11,550	t	A	11.55 A		
Chlorine	6,930	t	B	6.93 B		
Oxygen	Included in utilities and Invest.					
TOTAL RAW MATERIALS COST				38.61 Y + 11.55A + 6.93 B		
UTILITIES	Quantit	Unit	Price uc/unit			
Electricity	24,750	1000kwh	28	693		
Cooling Water	2,871	1000m ³	20	57,42		
Bl. Water		1000m ³				
Proc. Water		1000m ³				
steam Refrig.	4,752	ton	24	114.048		
Steam L. P.		l.ton				
Fuel	8,250	l.ton	70	577.5		
TOTAL UTILITIES COST				1,441.97	43.696	
OPERATING COSTS	Total men	Cost/year(uc)				
Labor	68	14,000		952		
Supervision	10	18,000		180		
Maintenance (Material and labor) (7% . TI)				3,500		
TOTAL OPERATING COSTS				4,632	140.363	
OVERHEAD EXPENSES						
Direct Overhead	30% LABO. COST			339.6		
General Plant overhead	65% OP. COST			3,010.8		
Insurance, Taxes	1.5%	TI		750		
Depreciation	10%	TI		5,000		
TOTAL OVERHEAD EXPENSES				9,100.4	275.769	
COST OF PRODUCTION				15,174.37 + 38.61Y + 11.55A + 6.93B		
BY PRODUCT CREDIT	Quantit	Unit	PRICE uc/unit			
				0		
				0		
TOTAL BY PRODUCT CREDIT						
NET COST OF PRODUCTION				15,174.37 + 38.61Y + 11.55A + 6.93B		
RETURN ON INVESTMENT 15% TI				7,500	227.272	
SALES EXPENSES						
TRANSFER PRICE				22,674.37 + 38.61 Y + 11.55A + 6.93B	687 + R.M.	

C- Chlorine route using ilmenite

We have considered the very hypothetical use of an Ilmenite feed.

The method of calculation employed in this case is the same as that used for the Richard Bay slag.

We have estimated a new value for the ratio "R" and we have applied this ratio to :

- the chlorine and coke consumptions
- 2/3 of the utilities consumptions (except oxygen)
- the investment calculation

The labor requirement remains the same as for the Richard Bay slag feed.

<u>COST OF PRODUCTION</u>					DATE: End 76		
<u>PRODUCT</u> TiO ₂ pigment			<u>CAPITAL INVESTMENT</u>				
<u>PROCESS</u> CHLORINE (Low grade R material)			<u>INSIDE BATT. LIMITS</u>				
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>				
<u>CAPACITY</u> 33,000 t/y			<u>TOTAL</u> 64 MUC				
<u>ON STREAM TIME</u> 8,000 h							
<u>RAW MATERIALS</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>	<u>Cost/year(mUC)</u>	<u>Cost/unit (uc)</u>		
Ilmenite 60%	59,400	t	Y	59.4 Y			
Coke	15,510	t	A	15.5 A			
Chlorine	33,000	t	B	33.0 B			
Oxygen	Included in Utilities and Invest.						
<u>TOTAL RAW MATERIALS COST</u> 59.4Y + 15.5 A + 33.0B					R.M.		
<u>UTILITIES</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>				
Electricity	42,000	1000kwh	28	1,176			
Cooling Water	4,880	1000m ³	20	97.6			
Bl. Water		1000m ³					
Proc. Water		1000m ³					
Refrig.	4,752	ton	24	114.05			
Steam L. P.		l. ton					
Fuel	14,025	l. ton	70	981.75			
<u>TOTAL UTILITIES COST</u>				2,369.4	71.8		
<u>OPERATING COSTS</u>	<u>Total men</u>	<u>Cost/year(uc)</u>					
Labor	70	14,000	980				
Supervision	10	18,000	180				
Maintenance (Material and labor)		7% -TI	4,480				
<u>TOTAL OPERATING COSTS</u>				5,640	170.9		
<u>OVERHEAD EXPENSES</u>							
Direct Overhead	30% LABO COST		348				
General Plant overhead	65% OP. COST		3,666				
Insurance, Taxes	1.5% TI		960				
Depreciation	10% TI		6,400				
<u>TOTAL OVERHEAD EXPENSES</u>				11,374	344.67		
<u>COST OF PRODUCTION</u> 19,387.4 + 59.4 Y + 15.5A + 33.0 B							
<u>BY PRODUCT CREDIT</u>	<u>Quantit</u>	<u>Unit</u>	<u>PRICE uc/unit</u>				
FeCl ₂ Fe Cl ₃							
<u>TOTAL BY PRODUCT CREDIT</u>							
<u>NET COST OF PRODUCTION</u> 19,387.4 + 59.4Y + 15.5A + 33.0B							
<u>RETURN ON INVESTMENT</u> 15% TI				9,600			
<u>SALES EXPENSES</u>							
<u>TRANSFER PRICE</u> 28,987.4 + 59.4Y + 15.5A + 33.0B							

2-4 TREATMENT PROCESSES

In this chapter we have evaluated the cost of the :

- ferrous chloride hydrolysis (HCl regeneration)
- Kel Chlorprocess (Cl₂ regeneration)
- sulfuric acid concentration (from 20% to 62.5%)
- complete treatment (Ref Treatment I)

The main steps of this treatment are copperas drying, strong acid concentration, Copperas and acid roasting, weak acid neutralization.

A- Ferrous chloride hydrolysis

The calculations are based on informations from the Woodall Duckham company.

- As an Australian site has been chosen the fuel price has been taken at 58 UC/t. If the fuel price were 70 UC/t. the cost of production would increase by about 3.5 UC/t HCl (100%)
- All the other assumptions remain the same as those in the previous calculation, except for the amortization which is over 7 years instead of 10 years
- It may be noted that the cost of the ferrous chloride hydrolysis is included in the economic calculations for the upgrading processes
- For a chlorine process based on low-grade Raw material, it may be noted that the production of 1 ton of TiO₂ pigment requires about 2 tons of Ilmenite and produces about 1,6 tons of iron chlorides which in turn yield give 1 ton of HCl and 0.87 ton of Fe₂O₃.

COST OF PRODUCTION				DATE: End 1976	
<u>PRODUCT</u> HCl 18.5%			<u>CAPITAL INVESTMENT</u>		
<u>PROCESS</u> Ferrous chloride hydrolysis (Woodall Duckham)			<u>INSIDE BATT. LIMITS</u>		
<u>LOCATION</u> AUSTRALIA			<u>OUTSIDE BATT. LIMITS</u>		
<u>CAPACITY</u> 31,000 t/y (exp. 100%)			<u>TOTAL</u>		3.3 M UC
<u>ON STREAM TIME</u> 8 000h					
<u>RAW MATERIALS</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>	<u>Cost/year muc.</u>	<u>Cost/unit (uc)</u>
Chlorides solution	137,600	m3		by product	
<u>TOTAL RAW MATERIALS COST</u>				by product	
<u>UTILITIES</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>		
Electricity	5,840	1000kwh	27	157.68	
Cooling Water	5.826	1000m ³	20	117.33	
Bl. Water	20	1000m ³	240	4.80	
Proc. Water	160	1000m ³		recycled	
Steam H. P.		l.ton			
Steam L. P.	(20,000)	l.ton		Fuel included	
Fuel	8,800	l.ton	58	510.40	
<u>TOTAL UTILITIES COST</u>				790.21	25.49
<u>OPERATING COSTS</u>	<u>Total men</u>	<u>Cost/year(uc)</u>			
Labor	10	12,000	120		
Supervision	1	18,000	18		
Maintenance (Material and labor)		7% TI	210		
<u>TOTAL OPERATING COSTS</u>				348	11.23
<u>OVERHEAD EXPENSES</u>					
Direct Overhead	30% LABO. COST		41.4		
General Plant overhead	65% OP. COST		226.2		
Insurance, Taxes	1.5% . TI		49.5		
Depreciation	15% . TI		495.0		
<u>TOTAL OVERHEAD EXPENSES</u>				812.10	26.20
<u>COST OF PRODUCTION</u>				1,950.31	62.92
<u>BY PRODUCT CREDIT</u>	<u>Quantit</u>	<u>Unit</u>	<u>Price uc/unit</u>		
Fe ₂ O ₃	28,000	t	0	0	0
<u>TOTAL BY PRODUCT CREDIT</u>				0	0
<u>NET COST OF PRODUCTION</u>				1,950.31	62.92
<u>RETURN ON INVESTMENT 20% TI</u>				660	21.29
<u>SALES EXPENSES</u>					0
<u>TRANSFER PRICE (exp HCl 100%)</u>				2,610.31	84.21

B- Kel Chlor process

The calculations are based on informations published by the Kellogg company.

(Ref Annex p A.21/A 22).

- The net cost of Cl_2 regeneration by this route is about 83 UC/t Cl_2
- If we consider the case of ferrous chloride regeneration in two steps, the total regeneration cost is

160 UC/t Cl_2 regenerated

When no treatment is required, it is not economic to regenerate these chlorides.

- In the case of an ilmenite feed the regeneration of the chlorides implies an overall cost of

(160 - X) UC/ton TiO_2 produced
where X is the Cl_2 unit price

e.g. with a Cl_2 price of 60 UC/t the cost of production of TiO_2 pigment with the ilmenite based chlorine process increases by about 100 UC/tonne.

COST OF PRODUCTION				DATE: End 76	
<u>PRODUCT</u> CHLORINE			<u>CAPITAL INVESTMENT</u> (uc)		
<u>PROCESS</u> KEL-CHLOR.			<u>INSIDE BATT. LIMITS</u>		
<u>LOCATION</u>			<u>OUTSIDE BATT. LIMITS</u>		
<u>CAPACITY</u> 25,000 t/y			<u>TOTAL</u> 4.15 MUC		
<u>ON STREAM TIME</u> 8 000h					
RAW MATERIALS	Quantit	Unit	Price uc/unit	Cost/year (muc)	Cost/unit (uc)
HCl (100%)	25,850	t	0	0	
Oxygen (99.5%)	5,775	t	30	173.25	
NaOH (50%)	70	t	50	3.5	
H ₂ SO ₄ (98%)	325	t	40	13	
TOTAL RAW MATERIALS COST				189.75	7.59
UTILITIES	Quantit	Unit	Price uc/unit		
Electricity	1,322.5	1000kwh	28	37.03	
Cooling Water	875.0	1000m ³	20	17.50	
Bl. Water	1,890	1000 m ³	240	0.45	
Proc. Water	1,229	1000 m ³	200	0.25	
Steam H. P.		l. ton			
Steam L. P.		l. ton			
Fuel		l. ton			
TOTAL UTILITIES COST				55.23	2.21
OPERATING COSTS	Total men	Cost/year(uc)			
Labor	8	14,000		112.0	
Supervision	1	18,000		18	
Maintenance (Material and labor) 7% TI.				290.5	
TOTAL OPERATING COSTS				420.5	16.82
OVERHEAD EXPENSES					
Direct Overhead	30% LABO. COST			39	
General Plant overhead	65% OP. COST			273.3	
Insurance, Taxes	1.5% TI			62.25	
Depreciation	10% TI			415	
TOTAL OVERHEAD EXPENSES				789.55	31.58
COST OF PRODUCTION				1,455.03	58.20
BY PRODUCT CREDIT	Quantit	Unit	Price uc/unit		
(80%) H ₂ SO ₄	339	t		0	
TOTAL BY PRODUCT CREDIT					
NET COST OF PRODUCTION				1,455.03	58.20
RETURN ON INVESTMENT 15% TI				622.5	24.90
SALES EXPENSES					
TRANSFER PRICE				2,077.53	83.10

C- Sulfuric acid concentration

The sulfuric acid is concentrated in a double effect evaporator.

The total investment includes the capital cost required for salt separation.

These plants are designed to concentrate sulfuric acid up to 62.5%. But there are other technologies, where sulfuric acid can be concentrated up to 95%.

When slag is used as raw material in the sulfate route, it is difficult to separate the salts. Even so, it seems probable that a Japanese company is at present developing a technology to treat such a waste acid.

In the cost calculation for the sulfuric acid concentration the water required for the ejectors is included in the cooling water consumption and the fuel cost is included in the steam price.

The sulfuric acid transfer price (with a return on investment of 15%) is 34.5 \$/Ton for a 62.5% acid, i.e.

55.2 \$/ton for a 100% acid.

Only a small amount of 62.5% sulfuric acid can be recycled in the TiO_2 process, but there are many other uses for such an acid : e.g. in fertilizer plants.

Despite this, we have assumed that this acid has no value, and so, the concentration step increases the TiO_2 cost of production by $(55.2 \times q)$ US\$/1ton TiO_2 pigment.

Where q is the free sulfuric acid content in the strong acid e.g. 1.4t of free sulfuric acid increases the TiO_2 price about 78 US \$/ton.

In cases where no copperas is produced at the salt content is low e.g. with a high grade raw material, the purer acid which contains little salt and no copperas could be concentrated at low cost.

COST OF PRODUCTION				DATE: End 76	
PRODUCT SULFURIC ACID 62.5% PROCESS VACUUM CONCENTR. OF SULFUR ACID LOCATION CAPACITY 105.600tH ₂ SO ₄ (62.5%) ON STREAM TIME 8 000h			CAPITAL INVESTMENT INSIDE BATT. LIMITS OUTSIDE BATT. LIMITS TOTAL 4.41 MUC (with filtration of salts)		
RAW MATERIALS	Quantit	Unit	Price uc/unit	Cost/year(m.uc)	Cost/unit (uc)
Sulfuric acid 300 g/l	220,000	m3		by-product	
TOTAL RAW MATERIALS COST					
UTILITIES	Quantit	Unit	Price uc/unit		
Electricity	1,900	1000kwh	28	53.2	
Cooling Water	14,254	1000m ³	20	285.08	
Bl. Water		1000 m ³			
Proc. Water	158.4	1000 m ³	200	31.68	
Steam H. P.		1 ton			
Steam L. P.	174,226	1 ton	6.4	1,115.05	
Fuel		1 ton			
TOTAL UTILITIES COST				1,485.05	14.06(50%)
OPERATING COSTS	Total men		Cost/year(uc)		
Labor	16		14,000	224	
Supervision	1		18,000	18	
Maintenance (Material and labor)	7%	TI		308.7	
TOTAL OPERATING COSTS				550.7	5.21 (18.5%)
OVERHEAD EXPENSES					
Direct Overhead	30%	LABO COST		72.6	
General Plant overhead	65%	OP. COST		3 57.9	
Insurance, Taxes	1.5%	TI		66.15	
Depreciation	10%	TI		441.00	
TOTAL OVERHEAD EXPENSES				937.65	8.88(31.5%)
COST OF PRODUCTION				2,973.36	28.16 (100%)
BY PRODUCT CREDIT	Quantit	Unit	Price uc/unit		
TOTAL BY PRODUCT CREDIT					
NET COST OF PRODUCTION				2,973.36	28.16
RETURN ON INVESTMENT 15% . TI				661.5	
SALES EXPENSES					
TRANSFER PRICE H ₂ SO ₄ 62.5%				3,634.86	34.42

D- Complete treatment

The "complete treatment" Ref Treatment I can be considered as an extrem solution since it is applied to a plant using a traditional technology and it does not take any advantage of a local context.

Nevertheless it can be interesting to keep in mind the main figures corresponding to this way as being extrem, values.

The main steps of this process are :

- Copperas drying
- Sulfuric acid concentration (without salts separation)
- copperas and sulfuric acid roasting
- sulfuric acid production
- weak acid neutralization

The increase of the cost of production is between 200 UC and 300 UC/1t TiO_2 pigment depending of the fuel and sulfur prices

COST OF PRODUCTION					DATE: En 76	
<u>PRODUCT</u> TREATMENT I			<u>CAPITAL INVESTMENT</u> (uc)			
<u>PROCESS</u> Treatment of the effluents from a			<u>INSIDE BATT. LIMITS</u>			
<u>LOCATION</u> 33 000t/y TiO ₂ plant (sulfate process)			<u>OUTSIDE BATT. LIMITS</u>			
<u>CAPACITY</u> R.M. Norw. Ilmenite			<u>TOTAL</u> 14,0 M UC			
<u>ON STREAM TIME</u> 8,000 h						
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/yea(m.uc)	Cost/unit (uc)	
Copperas and Waste acid				0		
<u>TOTAL RAW MATERIALS COST</u>						
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit			
Electricity	19,833	1000kwh	28	555.324		
Cooling Water	10,400	1000m ³	20	208.0		
Bl. Water		1000 m ³				
Proc. Water		1000 m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	40,590	l.ton	70	2,841.3		
<u>TOTAL UTILITIES COST</u>				3,604.6	109.23	
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)				
Labor	20	14,000		280		
Supervision	2	18,000		36		
Maintenance (Material and labor)	7%	TI		980		
<u>TOTAL OPERATING COSTS</u>				1,296	39.27	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30%	LABO. COST		94.8		
General Plant overhead	65%	OP. COST		842.4		
Insurance, Taxes	1.5%	TI		210.0		
Depreciation	10%	TI		1,400		
<u>TOTAL OVERHEAD EXPENSES</u>				2,547.2	77.19	
<u>COST OF PRODUCTION</u>				7,447.8	225.69	
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit			
Sulfur	34,320	t	65	2,230.8	67.6	
Ferric oxide + Misc	10,000	t	0	0		
<u>TOTAL BY PRODUCT CREDIT</u>				2,230.8		
<u>COST OF NEUTRALIZATION</u>				1,550	46.97	
<u>NET COST OF PRODUCTION</u>				6,767	205	
<u>RETURN ON INVESTMENT 15%</u>				TI	2,100	63.64
<u>TRANSFER PRICE</u>				8,867	268.7	

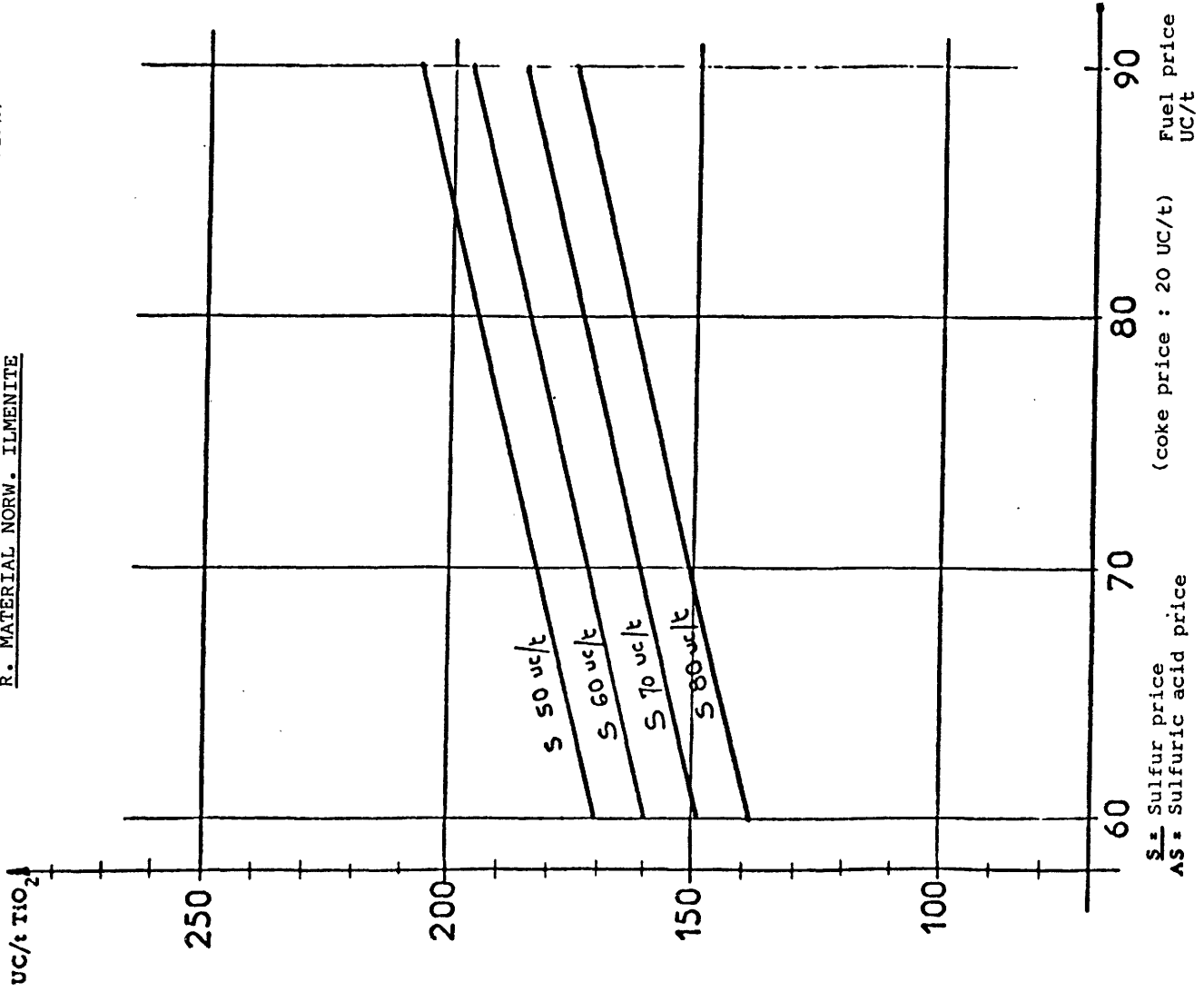
<u>COST OF PRODUCTION</u>					DATE: End 76	
TREATMENT I			<u>CAPITAL INVESTMENT</u>			
<u>PROCESS</u>	Treatment of the effluents from a 33 000t/y TiO ₂ plant (sulfate process)			<u>INSIDE BATT. LIMITS</u>		
<u>CAPACITY</u>	R.M. Canada Slag			<u>OUTSIDE BATT. LIMITS</u>		
<u>ON STREAM TIME</u>	8,000h			<u>TOTAL</u> 10.4M UC		
<u>RAW MATERIALS</u>	Quantit	Unit	Price uc/unit	Cost/year(muc)	Cost/t TiO ₂	
Waste acid				0		
<u>TOTAL RAW MATERIALS COST</u>						
<u>UTILITIES</u>	Quantit	Unit	Price uc/unit			
Electricity	5,166	1000kwh	28	144.648		
Cooling Water	6,859	1000m ³	20	137.18		
Bl. Water		1000m ³				
Proc. Water		1000m ³				
Steam H. P.		l.ton				
Steam L. P.		l.ton				
Fuel	26,400	l.ton	70	1,848.00		
<u>TOTAL UTILITIES COST</u>				2,129.82	64.54	
<u>OPERATING COSTS</u>	Total men	Cost/year(uc)				
Labor	12	14,000		168		
Supervision	2	18,000		36		
Maintenance (Material and labor)	7%	TI		728		
<u>TOTAL OPERATING COSTS</u>				932	28.24	
<u>OVERHEAD EXPENSES</u>						
Direct Overhead	30% LABO COST			61.2		
General Plant overhead	65% OP. COST			605.8		
Insurance, Taxes	1.5%		TI	156		
Depreciation	10%		TI	1040		
<u>TOTAL OVERHEAD EXPENSES</u>				1,863	56.45	
<u>COST OF PRODUCTION</u>				4,924.8		
<u>BY PRODUCT CREDIT</u>	Quantit	Unit	Price uc/unit			
Sulfur	19,800	t	65	1,287	39	
Ferric oxide + Mis	47,000	t	0	0		
<u>TOTAL BY PRODUCT CREDIT</u>				1,287		
<u>COST OF NEUTRALIZATION</u>				1,550	46.97	
<u>NET COST OF PRODUCTION</u>				5,187.82	157.21	
<u>RETURN ON INVESTMENT 15% PI</u>				1,560	47.27	
<u>TRANSFER PRICE</u>				6,747.82	204.48	

COST OF TREATMENT UC/t TiO₂

TREATMENT I (EUR 5195 f)

Cost with amortization but without return on Invest. +60UC/t TiO₂ (15%)

R. MATERIAL NORW. ILMENITE



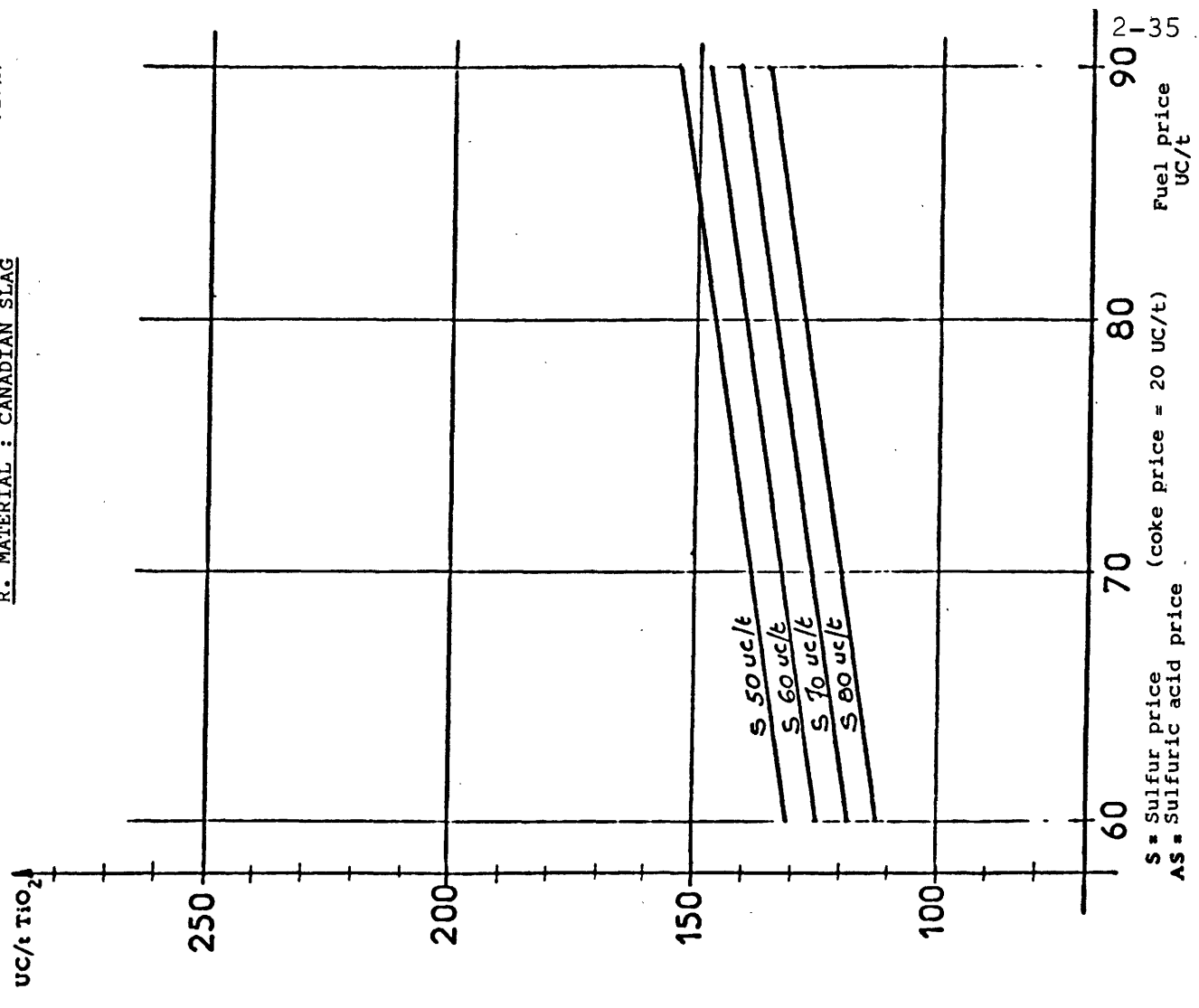
S = Sulfur price (coke price : 20 UC/t)
AS = Sulfuric acid price

COST OF TREATMENT UC/t TiO₂

TREATMENT I (EUR 5195f)

Cost with amortization but without return on Invest. +44UC/t Ti (15%)

R. MATERIAL : CANADIAN SLAG



S = Sulfur price (coke price = 20 UC/t)
AS = Sulfuric acid price

2-5 RAW MATERIAL ECONOMICS

In this chapter we have analyzed the relative positions of the main minerals ores available in respect of their economic effect on the TiO_2 cost of production.

These analyses have been done without considering the effect on environment. This has been done separately in a previous chapter.

We have analysed 5 cases in which we have determined ...

	FIGURES	...DETERMINATION ... WHICH WOULD YIELD THE OF A THEOTICAL PRICE OF...	SAME COST OF PRODUCTION (TiO_2 pigment) as
Case 1	2-2,2-3, 2-4	Rutile (Nat or Synth) used in chlorine pro- cess	Ilmenite used in sulfate process
Case 2	2-5	Rutile (Nat.or Synt used in chlorine process	Ilmenite used in chlorine process
Case 3	2-6	Synthetic rutile used in sulfate process	Slag (70%) used in sulfate process
Case 4	2-7	Slag 85% used in sulfate process	Ilmenite used in sulfate process
Case 5	2-8	Slag 70% used in sulfate process	Ilmenite used in sulfate process

These figures relate the price of one feedstock transformed in a first process to the price of an other feedstock transformed in a second process which would yield the same cost of pigment production.

Example :

When we are in the position where a theoretical price of rutile at 140 UC/t gives the same cost of production in the chlorure process as ilmenite does at 35 UC/t in the sulfate process the use of rutile at a commercial price of 200 UC/t implies an increase in the cost of production of : $(200-140) \times 1.2 = 72\text{UC/t TiO}_2$ pigmt.

weight of Rutile/1ton TiO_2

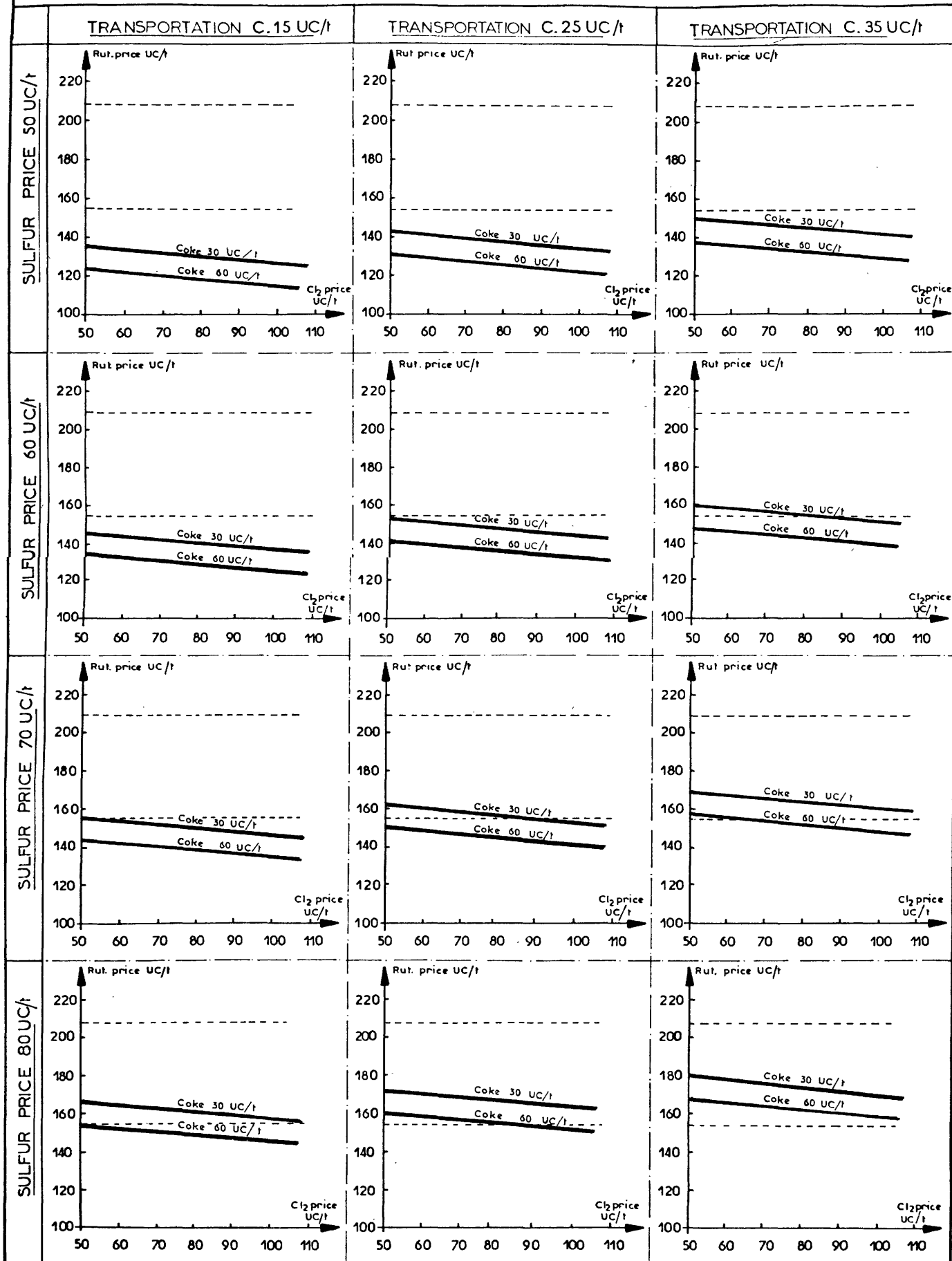
This increase in cost may be offset by the environmental advantage of this process. The calculation of these theoretical prices is based on the economic calculations we developed in the previous chapter and by variation of the main parameters :

- Ilmenite price 30-60 UC/t (c.i.f.)
- Chlorine " 50-110UC/t
- sulfur " 50-80 UC/t
- Coke " 30-60 UC/t
- Slag 70% " 70-110UC/t (c.i.f.)

THEORETICAL PRICE OF FEEDSTOCK USED IN THE CHLORINE PROCESS WHICH WOULD YIELD THE SAME COST OF PRODUCTION AS THE ILMENITE BASED SULFATE ROUTE

(TRANSFER PRICE RANGE OF S. RUTILE IS SHOWN BY THE DASHED LINES)

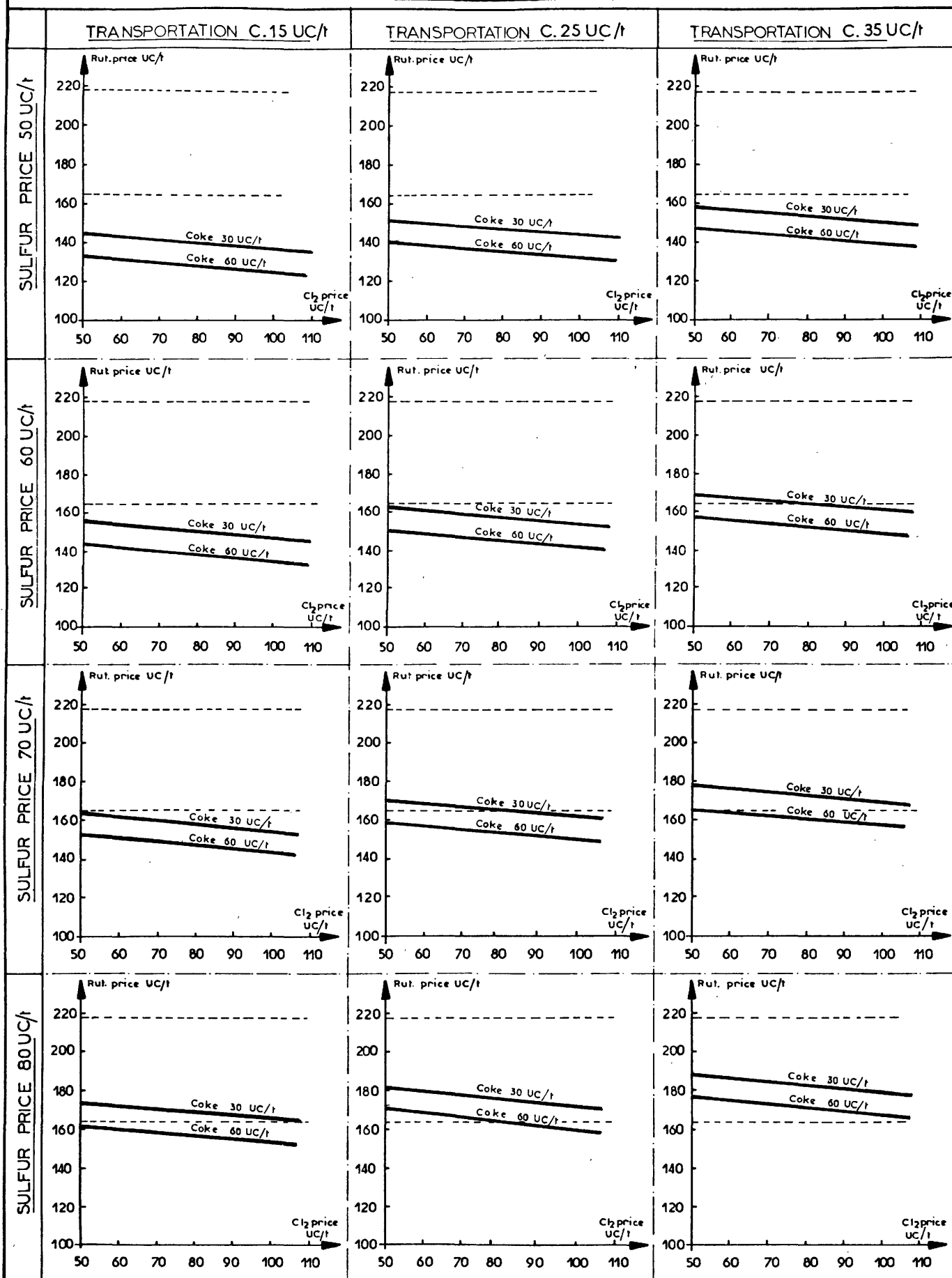
ILMENITE PRICE 15 UC/t



THEORITICAL PRICE OF FEEDSTOCK USED IN THE CHLORINE PROCESS WHICH WOULD YIELD THE SAME COST OF PRODUCTION AS THE ILMENITE BASED SULFATE ROUTE

(TRANSFER PRICE RANGE OF S. RUTILE IS SHOWN BY THE DASHED LINES)

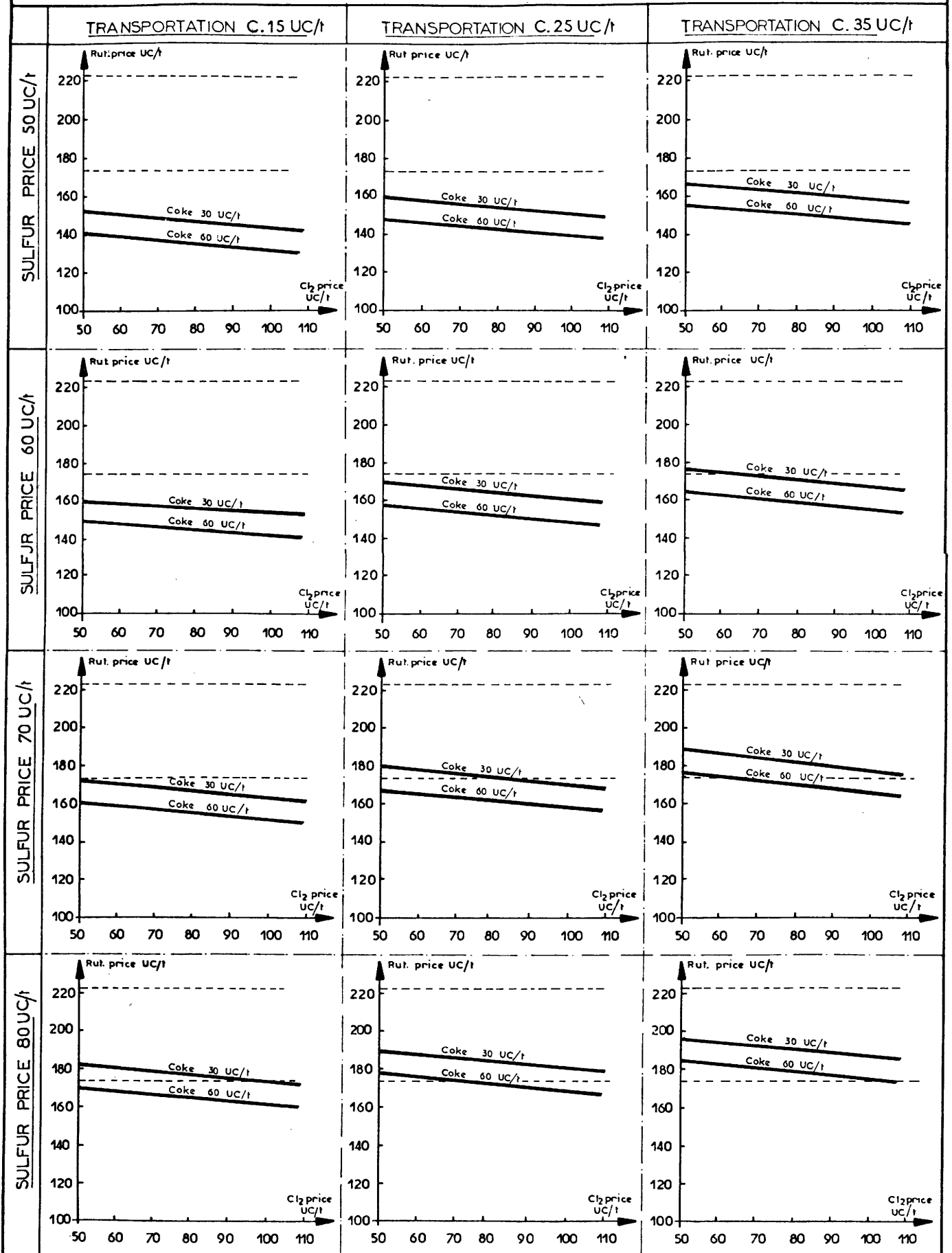
ILMENITE PRICE 20 UC/t



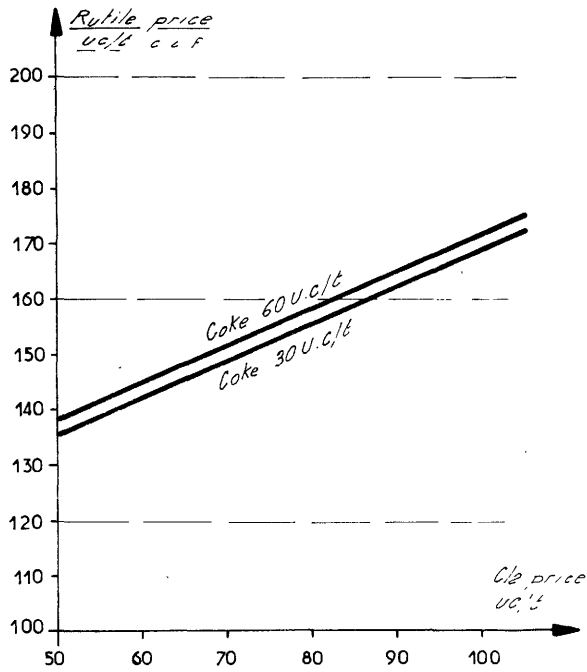
THEORETICAL PRICE OF FEEDSTOCK USED IN THE CHLORINE PROCESS WHICH WOULD YIELD THE SAME COST OF PRODUCTION AS THE ILMENITE BASED SULFATE ROUTE

(TRANSFER PRICE RANGE OF S. RUTILE IS SHOWN BY THE DASHED LINES)

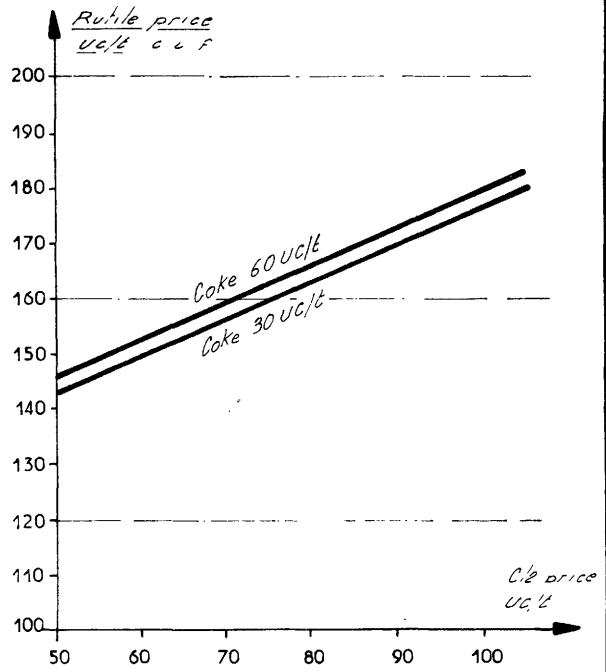
ILMENITE PRICE 25 UC/t



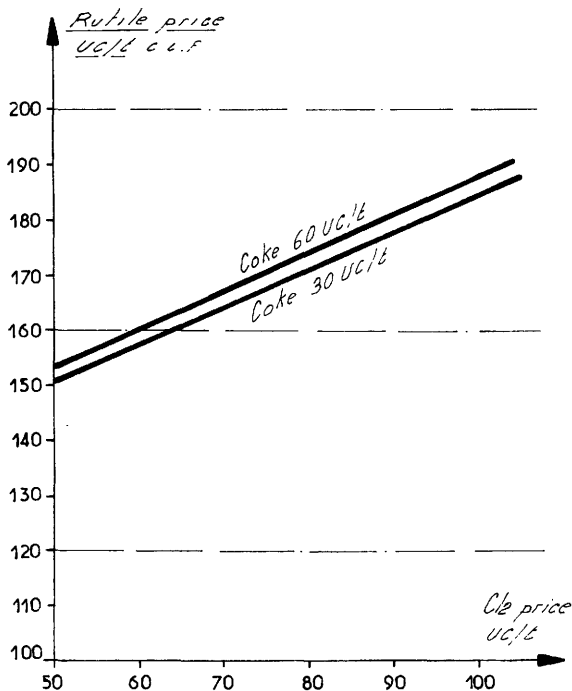
Theoretical price of Rutile used in the chlorine process which would yield the same cost of production as the ilmenite based chloride route
 (no cost of treatment included)



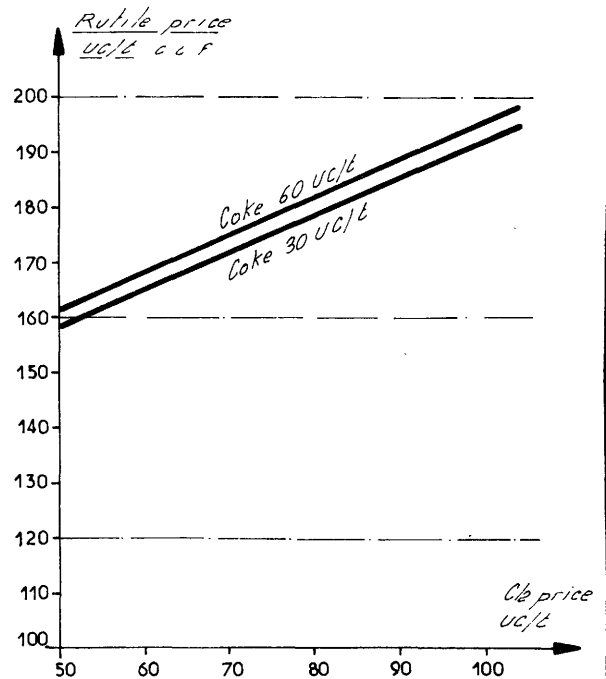
ILMENITE 25 UC/t (c.i.f)



ILMENITE 30 UC/t (c.i.f)



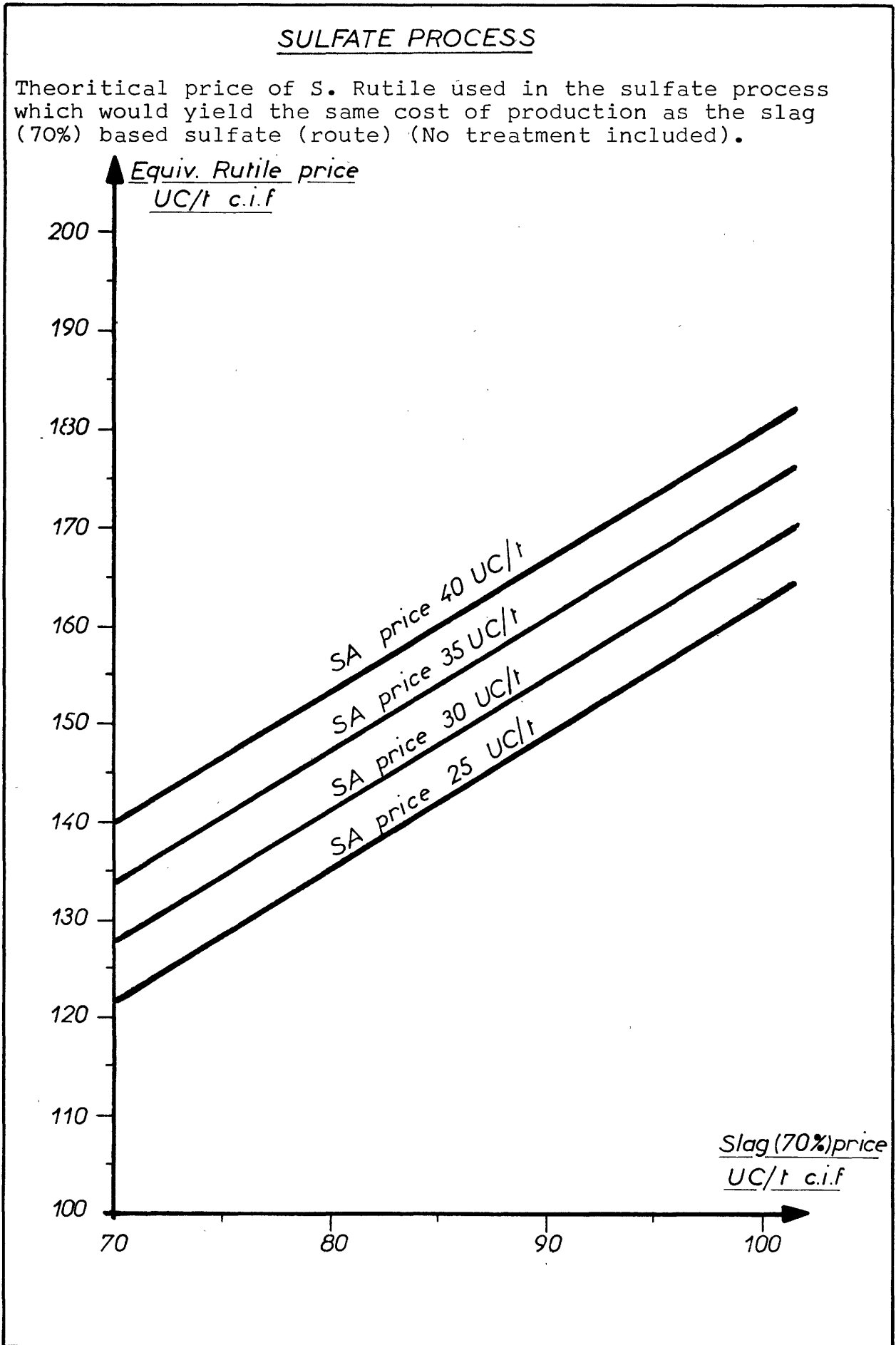
ILMENITE 35 UC/t (c.i.f)



ILMENITE 40 UC/t (c.i.f)

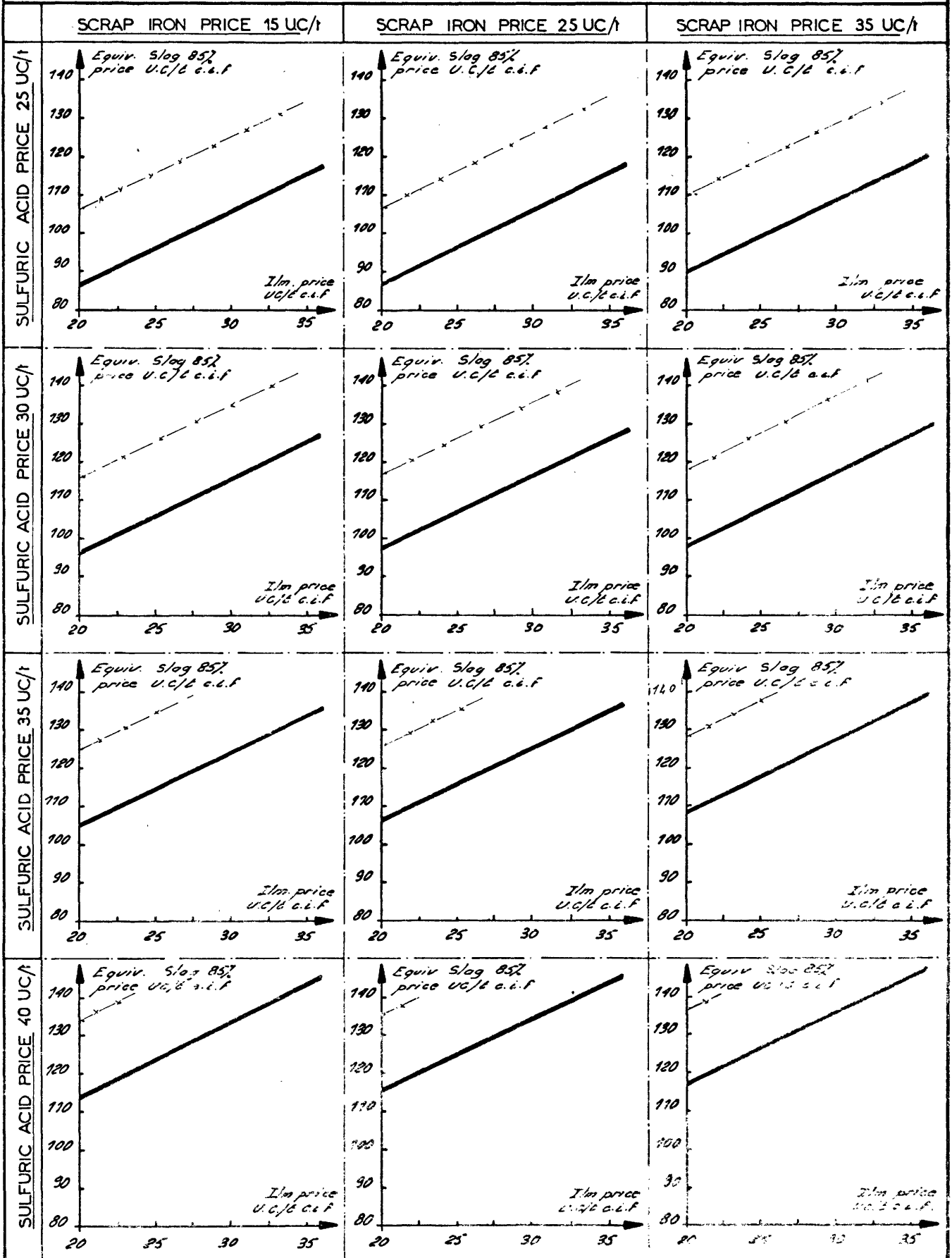
FIGURE 2-6

CASE 3



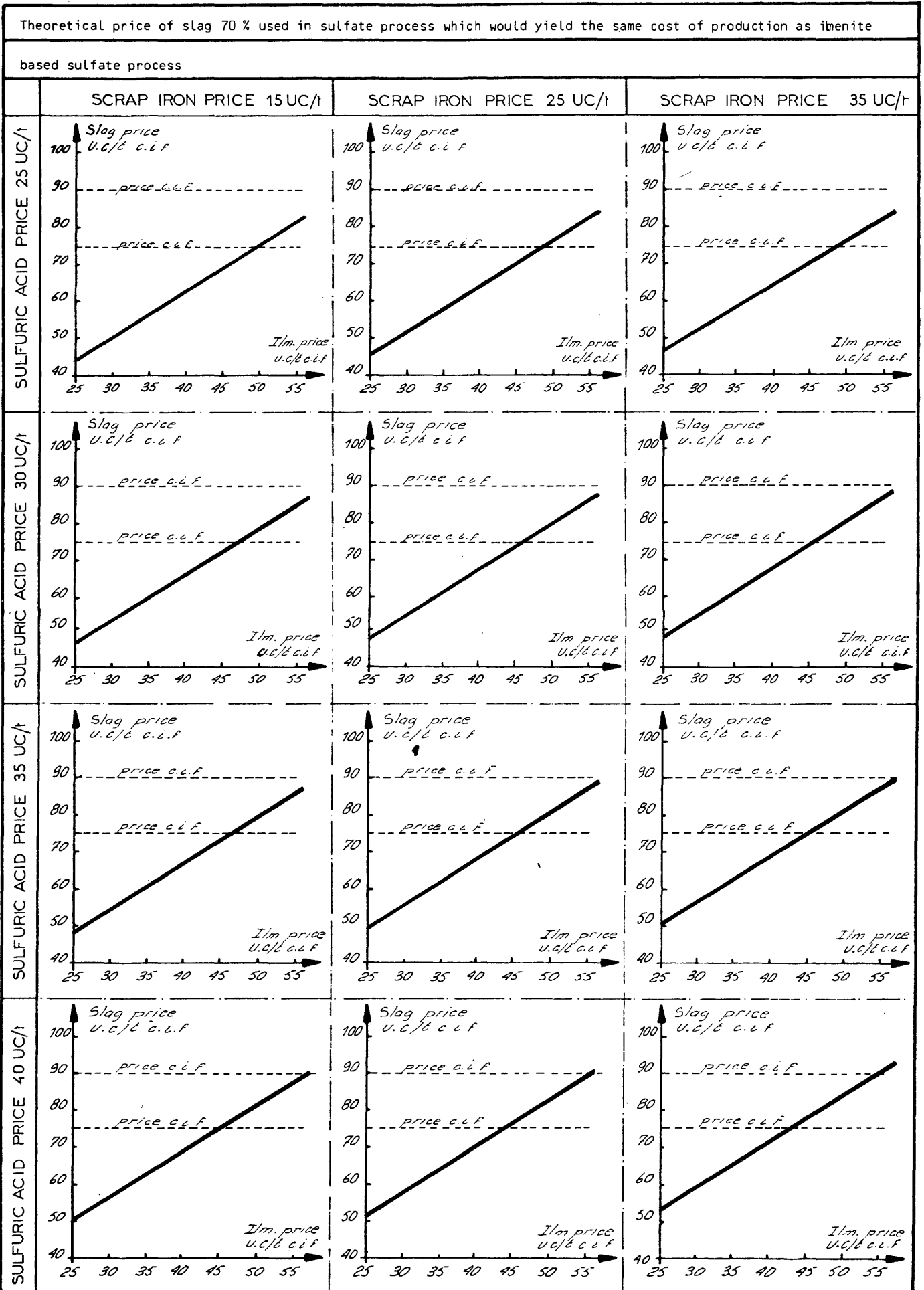
CASE 4

Theoretical price of slag 85% used in sulfate process which would yield the same cost of production as ilmenite based sulfate process



NB1 No cost of treatment included

NB2 the dashed---line corresponds to the advantage due to the lower investment required.



NB 1 No cost of treatment included

NB 2 The dashed \rightarrow line corresponds to the advantage due to the lower investment required

SECTION 3

SYNTHETIC RUTILE INDUSTRY

SECTION 3

SYNTHETIC RUTILE INDUSTRY

3-1 Introduction

3-2 Technical context

Table 3-1 "Summary of the synthetic Rutile situation"

Figure 3-1 "Upgrading processes"

Table 3-2 Examples of extraction capacity of the main upgrading processes

3-3 Main Realizations and projects

3-4 Environmental impact

3-5 Licensing Policy

3-1 INTRODUCTION

For a long time the synthetic Rutile industry has been considered as particularly undecided. These hesitations stood in contrast with an apparent economic incentive.

At the beginning these hesitations could be partially imputed to some technical difficulties, but now some processes seem to be well proved and the analysis of the present situation must be done on general economic bases.

A short description of the technical context is presented in the next chapter (3-2). This description does not include any exhaustive analysis of each upgrading process, since it has been published many times before ; however the original aspects of each process have been pointed out.

The main data concerning raw materials and utilities consumptions are given in the same chapter whereas the economic calculations are developed in an other section (Economic analysis).

The main realizations and the main projects are presented in chapter 3.3 and the specific context of each case is analyzed in order to find out whether or not a given case can be considered as being an example.

Finally, the environmental impact of the various processes is considered in the last chapter, e.g. 3,4.

3-2 TECHNICAL CONTEXT

Although there is a lot of upgrading processes we have selected only eight processes, as being the most representative of their categories.

Many other types of processes have been developed out have never been tested on an industrial or pilot scale.

A schematic description of these eight processes is given in figure 3-1 and some indications dealing with the type of process, the by-products the realizations, the projects and the relevant patent references are given in table 3-1.

The first part of table 3-1 corresponds to the processes which have been developed on an industrial scale and the second part gives the processes which have been developed on a pilot scale only.

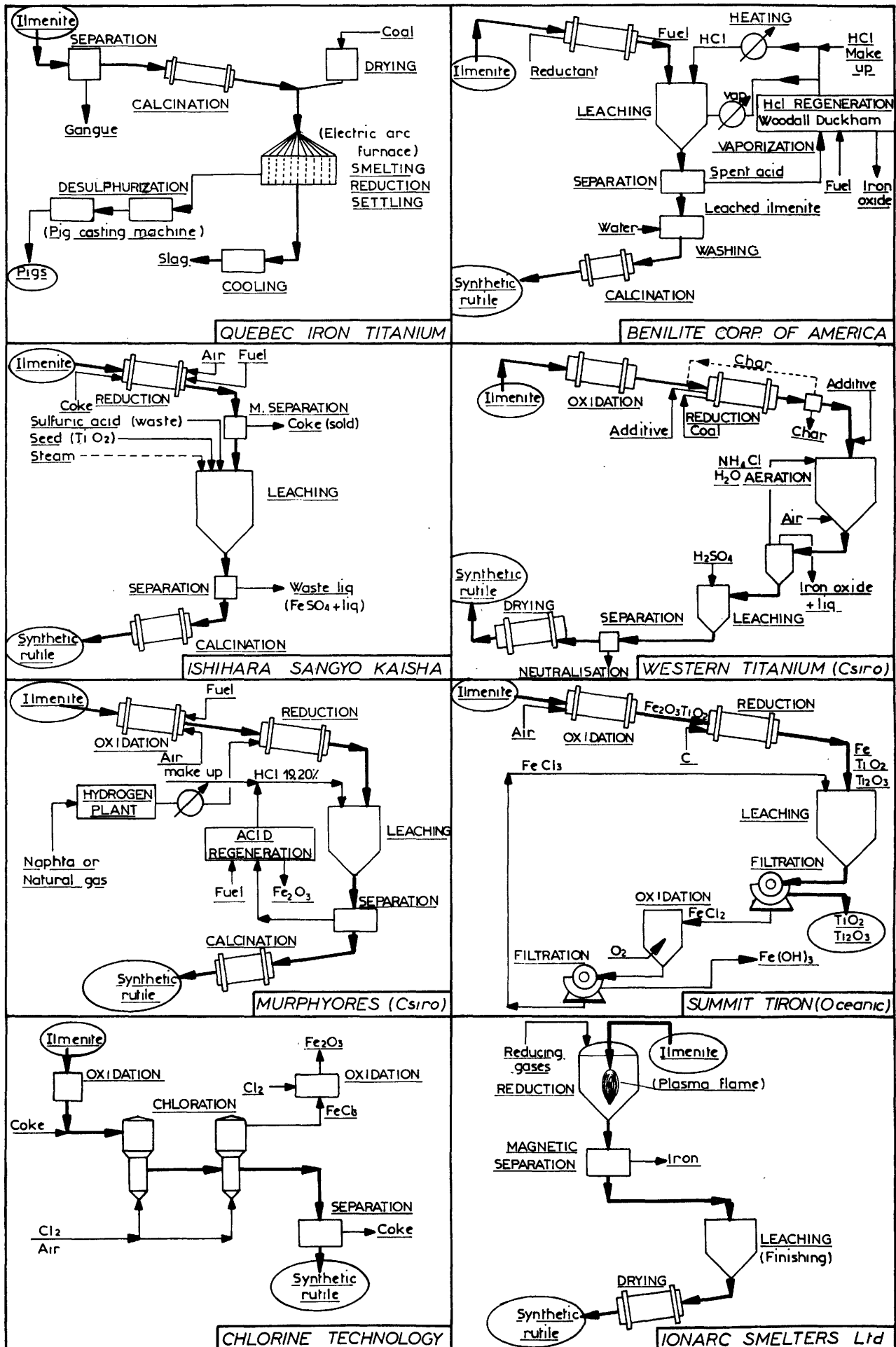
The total capacity (End 1976) of the synthetic rutile plants is about 240,000 tpa for the chemical processes and 850.000tpa (70%TiO₂) for the slag process.

TABLE 3-1
SUMMARY OF THE SYNTHETIC RUTILE SITUATION (end 1976)

Companies having developed their own process	Type of process	by product	Realizations Company Capacity Location	Projects	Patents	Remarks
BENELITE CORP OF AM (U.S.A.) Ref 2	Reduction Leaching (HCl) Calcination	FeCl ₂ (Cl ₃) in solution 20-23 %	Taiwan Alkali 30.000 tpa Rut (Taiwan) Malaysian Tit. Corp. 60.000tpa(Rut) (Malaysia) Kerr Mcgee 50.000tpa(Rut) (USA)	-Kerala Min. 30.000 tpa (India) 1980 -Indian Rare earth 50.000tpa 1980 (India). Sakai 30.000tpa (Japan) Vuorikemiaoy (Finland)	US 3.193.376 (Wah Chang. Corp) US 3.825.419	- Using Wah Chang technic Benilite Corp was during many years the alone company to commercialize an upgrading process
DHRANGADHRA CHEM.WORKS Ltd (India)	Reduction Leaching (HCl) Calcination	FeCl ₂ (-Cl ₃) in solution	Dhrangadhra 20-30.000tpa (exp Rutile) (Indian)	No extension planned	Initially. Wah Chang	- the Dhrangadhra plant was constructed with the wah chang technic. Presently his company has developed its own know-how
ISHIHARA Sangyo Kaisha Ltd (Japan) Ref 3	Reduction Leaching (H ₂ SO ₄) Calcination	FeSO ₄ in solution	Ishihara 43.000 tpa (Rut.) (Japan)		US 3.660.078	- Very recently this company is believed to have decided to sell its license.
Q.I.T. (Canada) Ref 1	Slag.	"Fe"	Q.I.T. 850.000 tpa (70% TiO ₂) (Canada)	In South Africa 400.000tpa (85% TiO ₂) 1978	US3.428.427 (Leaching tech.) US2.919.982 US2.853.375	-400.000 tpa is a minimum size for this type of process
WESTERN TITANIUM (Australia) Ref 4	Oxydation Reduction Aeration Leaching Drying	Fe ₂ O ₃	Western Titanium 36.000 tpa (Rut.) Australia	Two projects (location not available)	Brit. 1.186.522 (+CSIRO)	-This company might be willing to license its process and might a joint venture project.
MURPHYORES (Australia) Ref 5	Oxidation Reduction Leaching (HCl) Calcinat.	FeCl ₂ (-Cl ₃) in solution	Mitsubishi Chem. Pilot (Japan) Presently Shut down		US3.922.164 (+CSIRO) US3.929.963 (+Mitsubishi Chemical)	-This company could license its process
SUMMIT-TIRON (USA) Ref 6	Oxidation Reduction Leaching (FeCl ₃)	FeCl ₂ in solution	Summit.Tiron Pilot (Canada) Presently dismantled	No project	US3.252.787 (Oceanic Proc. Corp.)	-This company has terminated its process development
GULF CHEMICAL (USA)	Reduction Leaching (HCl)	FeCl ₂ in solution	Gulf.Chem. pilot 10.000 - 40.000 tpa presently shut down		Wah chang ? process	
CHLORINE TECHN. Ref 7	Selective Chlorination	FeCl ₃	Rutile and Zircon Pilot	This company which is a subsidiary of Rutile and Zircon had agreement with Sherwin William and then with AKZO but the process is not again commercially developed		
IONARC SMELTERS Ltd Ref 8	Plasma reduction Leaching		Partial tests on reduction step			
MITSUBISHI MINING (Japan)	Selective chlorination	FeCl ₃	Mitsubishi Mining Pilot (Japan)	Construct. of a bigger Pilot	As chlorine tech. and DuPont this company has run into many difficulti due to the continuous character of the process and the oxidation step	
DuPONT TIOXIDE(BTP) NATIONAL LEAD THANN & MULHOUSE BAYER	Selective Chlorination.				GERM. 1.941.509 FR.2.015.642 US 3.529.933 FR 1.566.670 GERM. 1.211.136	It can be considered that all the main pigment producers have developed the technology of ilmenite upgrading

Figure 3.1

UPGRADING PROCESSES



EXAMPLES OF THE EXTRACTION CAPACITY OF THE MAIN
UPGRADING PROCESSES

It is obvious that for a given process, the characteristics of the synthetic Rutile are closely related to the characteristics of the raw ilmenite. It is the reason why we have put in front of each composition of synthetic rutile obtained by some upgrading processes, the composition of the supposed raw ilmenite.

It should be noted that the extracted fraction must be considered as relative indications.

MURPHYORES PROCESS					Comm. name of product. "MURUTILE"
	S. Rutile % wt	Ilm. Aust East C	Ilm. requ. kg/100kg	extract. fract. %	
TiO ₂	96.2	52.9	101.26	R	
FeO		30.8	58.9		
Fe ₂ O ₃	1.5	11.9	22.78	98	
SiO ₂					
Cr ₂ O ₃	0.15	0.14	0.27	44	
CaO	(0.01)	0.05	0.10	90	
Al ₂ O ₃	0.23	0.25	0.48	52	
V ₂ O ₅	0.04	0.16	0.31	87	
MnO	0.05	1.77	3.39	98	
MgO	0.04	0.54	1.03	96	

MURPHYORES PROCESS					Comm. name of product. "MURUTILE"
	S. Rutile % wt	Ilm. Aust West C	Ilm. req. kg/100kg	Extract. fract. %	
TiO ₂	95.5	54.5	101	R	
FeO	-	23.7	43.92		
Fe ₂ O ₃	1.2	17.2	31.88	98	
SiO ₂	1.0	0.5	(0.93)	0	
Cr ₂ O ₃	0.02	0.04	0.07	71	
CaO					
Al ₂ O ₃	0.2	0.8	1.48	86	
V ₂ O ₅	0.06	0.4	0.74	92	
MnO	0.05	1.7	3.15	98	
MgO	0.05	0.4	0.74	93	

ISHIHARA S.K. PROCESS					Comm. name of product. "RIIPAOIE"
	S. Rutile % wt	Ilm. Ind. Q. C.	Ilm. requ.	extract. fract. %	
TiO ₂	96.1	60.3	100.7	R	
FeO		9.7	16.2		
Fe ₂ O ₃	1.7	24.8	41.4	97	
SiO ₂	0.5	1.4	2.34	79	
Cr ₂ O ₃	0.15	0.14	0.23	35	
CaO	0.01	0.15	0.25	96	
Al ₂ O ₃	0.46	1.0	1.67	72	
V ₂ O ₅	0.20	0.26	0.43	53	
MnO	0.03	0.40	0.67	96	
MgO	0.07	0.65	1.09	94	

WAH CHANG CORP. PROCESS.				
	S. Rutile % wt	ilmenite %wt	ilmenite req.	Extract. fract. %
TiO ₂	93.00	54.44	98	R
FeO	0.32	23.54	42.37	
Fe ₂ O ₃	3.70	18.37	33.07	91
SiO ₂	1.02	0.56	1.01	0
Cr ₂ O ₃	0.05	0.03	0.05	0
CaO				
Al ₂ O ₃	0.11	0.72	1.30	92
V ₂ O ₅	0.04	0.05	0.09	56
MnO	0.02	1.59	2.86	99
MgO	?	?		?

SLAG PROCESS				
	S. Rutile % wt	Ilm. A. take	Ilmenite required	Extract. fract. %
TiO ₂	71	34.3	74	R
FeO	13.5	27.5	59.33	
Fe ₂ O ₃	-	25.2	54.37	86
SiO ₂	4.25	4.3	9.28	54
Cr ₂ O ₃	0.25	0.1	0.22	0 ?
CaO	1.2	0.9	1.94	38
Al ₂ O ₃	5.0	3.5	7.55	34
V ₂ O ₅	0.55	0.27	0.58	5
MnO	0.23	0.15	0.35	29
MgO	5.0	3.10	6.69	25

BENILITE

No information available

WESTERN TITANIUM

The Western Titanium process can only extract Iron and Manganese

- BENELITE CORP. OF AM. (Ref 2)

The Benelite process is derived from the wah Chang process.

The main steps of this process are :

- reduction (Coke)
- Leaching (HCl)
- Separation of the rutile from the ferrous chloride solution
- calcination
- Recycling of the HCl by ferrous chloride hydrolysis (Woodall Duckkam process)

For some Ilmenite with a small oxygen content not enough oxidized (Rocky deposit) it could be necessary to add an oxidizing step.

It is difficult to know the extractive performance of this process and consequently the restriction concerning the raw material, but many tests have been carried out on Ilmenite from India, USA, Norway, Australia, South Africa, Finland. The low TiO_2 content (Finland) is not a restriction as far as the technical aspect is concerned. Although the Wha Chang process has a poor chromium extractive power, the Benilite seems to be able to use raw materials with a relatively high chromium content.

Presently the plants in operation are using :

- Indian Ilmenite (Q grade) in Taiwan
- Malaysian Ilmenite in Malaysia
- Australian Ilmenite in USA (K.Mc Gee)(US Ilmenite in the future)

It must be noted that the Indian ilmenite Q grade has a very good oxidation level but also a relatively high chromium content (table 4-2 section 4).

(Concerning) the main consumptions given in the literature (or by the producers is as follows (/1t S.Rutile)

Ilmenite (55% TiO_2)	1.83 t
Make up HCl (31.5%)	0.15 - 0.26
Fuel (No6)	0.54t (HCl regen.incl.)
Steam	1.25 t
Electricity	300 - 390 Kwh
Cooling water	12m3
Labor requirement	12 men/shift
Supervision	3 men

The investment for a 100,000 t/y (Synthetic Rutile) plant ranges from 22 MUC to 32 MUC (depending of the location).

For example a plant located in Malaysia, costs 22 MUC whereas a plant located in USA requires a 32 MUC capital expenditure.

It must be noted that some parts of the plant have a maximum size corresponding to a 30 000 t/y capacity, hence the estimation of the total investment for various capacities must not be done only with (scaling factors).

An other point is that in some locations the investment advantage due to the location can greatly modified by the number of import item and by the time required for realization.

This process is known to be very reliable ; this means that it can implemented in any country even in non industrialized zones.

- Q.I.T.

Quebec Iron Titanium has developed a slag process, such a process has also been developed by Japanese and Russian producers.

The main steps of this process are :

- calcination
- smelting with reduction and settling
- Cooling of the slag fraction
- desulfurization of the iron fraction

Concerning the usable raw material, it must be noted that some metal oxides are soluble in both the iron fraction and slag fraction and this can limit the quality of the final product.

As far as the chloride process is concerned, the canadian ilmenite and more generally the rocky ilmenite with a high CaO and MgO content yields a lower grade slag.

The Richard Bay product is based on a sandy Ilmenite with a relatively low TiO_2 content but without too many troublesome impurities.

The chromium content can be reduced by a pretreatment (leaching ?) before the slag process.

The main consumptions of this process are :

electricity	about 3600 Kwh (t slag 70% TiO_2)
coke	0.3t/t slag 70% TiO_2

CO (0,7/t) is obtained as a by-product and is used locally as fuel.

Running such a process requires a very good know-how and presently Q.I.T is the only company operating a large scale plant.

The TiO_2 content of the product is a very important factor as far as the reliability of the process is concerned. A slag with a high TiO_2 content becomes more refractory and needs higher temperatures, more sophisticated equipment and more stringent operating conditions. For the Richard Bay project, Q.I.T has estimated that a TiO_2 content of 85% could be considered as being a good compromise.

- ISHIHARA SANGYO KAISHA

This Japanese company which produces TiO_2 by the sulfate route has developed a process based on leaching with sulfuric acid (waste acid).

The main steps of this process are :

- reduction
- leaching (H_2SO_4)
- separation of the rutile from the ferrous sulfate solution
- calcination

As I.S.K. uses the leaching solution in an other plant, this process does not include a regeneration step but this one could be feasible.

I.S.K. operates the unique plant based on this process and uses Indian ilmenites (Q grade) which have a high chromium content, some vanadium and some SiO_2 .

Ilmenite with a lower Fe^{+++}/Fe^{++} ratio can imply the addition of an oxidation step. SiO_2 content can also be a limitation.

As the vanadium content of the Q grade is relatively high, it can be considered that this element does not represent a very stringent constraint for this process.

The main consumptions (/1t S. Rutile) of this process are :

Ilmenite	1.83 t
Coke*	0.095t
Sulfuric acid	1.9 t
Electricity	300 Kwh
C.Water	12 m3
Fuel	0.34 t

(*Coke must be used in excess. The excess cannot be recycled because some impurities contained in the fresh coke are necessary for the process)

Labor requirement : 9 men/shift

Supervision : 3 men

No specific information dealing with the investment are available. It seems that good order of magnitude could be 22 MUC for a 100.000 t/y (rutile) plant (located in Japan).

- WESTERN TITANIUM (Australia)

Western Titanium is an Ilmenite producer located on the Australian West coast. The process has been developed with the C S I R O.

The main steps of this process are :

- oxidation
- reduction (coal)
- aeration
- separation of the ferric oxide
- leaching (for completion of the extraction)
- drying

The extractive power of this process is limited to Iron and Manganese.

This poor extraction power could be a limitation for this process but in Australia (W. coast) large reserves of Ilmenite having an adequate quality are available.

The main consumptions (/1 ton S. Rutile) of this process are :

- ilmenite (Eneabba)	1.9t
- coal	0.8t
- ferrous sulfate	0.18t
- am.chloride	0.012t
- sulfuric acid	0.06t
- limestone	0.08t
- electricity	190 Kwh
- Fuel (oxidation)	0.056t
(drying)	0.019t
Water	16m3

The investment for a 100.000t/y (Synthetic Rutile) plant located in Australia is about 22 MUC.

It must be noted that (as for many other processes) the capacity depends on the quality of the ilmenite. For example, the same plant can produce 54.000t/y of S.Rutile when based on ilmenite from Capel and 68.000t/y when based on Ilmenite from Eneabba

This process is known to have had some trouble with the quality of product. It seems that at the beginning only Du Pont was able to use this S.Rutile as raw material.

Presently the quality has been improved and a new plant having a capacity of 36,000t/y is in operation in Capel. This capacity will be 57,000t/y in 1977 when switching of raw material.

The operation of this process does not seem very easy and it could be a drawback for the installation of this process in some locations.

- MURPHYORES (Australia)

Murphyores is a Rutile producer located on the Australian East Coast ; the process has been developed with C.S.I.R.O.

The main steps of this process are :

- oxidation
- reduction
- leaching
- separation of S.Rutile
- calcination
- regeneration of the HCl

The extractive power of this process is good, and allows the use of ilmenite with a relatively high chromium content such as the Australian East coast ilmenite.

The main consumption (/1t S. Rutile) of this process are :

- | | |
|---------------|---------------------|
| - ilmenite | 1.83t |
| - HCl (100%) | 0.15t |
| - hydrogen | 150 Nm ³ |
| - electricity | 300Kwh |
| - fuel | 0.5t |
| - water | 8m ³ |

No specific investment figure is available, but the economic calculation have been based on the same investment as for the Benilite process. This total investment does not include hydrogen generation which is taken care of in the price of hydrogen.

No industrial plant is on stream but this process has been tested for a long time in a pilot plant built by Mitsubishi Chemical in Kurosaki (Japan).

This pilot plant has been shut down in 1975 after the completion of the test program.

No precise information concerning the pilot runs have been published.

- DHRANGADHRA CHEM WORKS

In fact the Dhrangadhra chem. W plant is based on the wha chang process, but during the five years of operation (start up : 1971) the indian company has made many improvements over the original process and consider having its own know-how.

No specific details concerning this plant are available.

Presently the leaching solution is dumped but will be treated (W.D. process) in 1978 for economic reasons.

Dhrangadhra estimates that the total cost of their 20.000 t/y S.R. plant was about 2 MUC (1971).

- SUMMIT-TIRON

Tiron is a subsidiary of Summit. The process which has been tested in Canada by this company is the Oceanic Corp process.

The main step of this process are :

- oxidation
- reduction
- leaching (FeCl_3)
- oxidation
- FeCl_3 recycling

A part from the patent description it is difficult to have any specific information.

The pilot which was built in Canada is presently dismantled but we do not know the exact conclusions of the runs presently it seems difficult for this company to commercialize this process without having a pilot plant in operation.

CHLORINE TECHNOLOGY

Chlorine Technology is a subsidiary of Rutile and Zircon Mines (Australia).

Basically this process is a selective chlorination of ilmenite.

The main steps are :

- oxidation
- chlorination
- separation of the S. Rutile
- Oxidation of the chlorides (Cl_2 regeneration)

This continuous process is very difficult to operate and the oxidation step does not seem to be working properly yet ; Rutile and Zircon Mines does not consider that this process can be commercialized at the present time.

Mitsubishi Metal (Japan) and Du Pont have also met this type of difficulties.

It must be noted that for this type of process a location near a TiO_2 chloride plant seems to be optimum.

This process can use a wide range of Ilmenite grades as raw material ; however a substantial vanadium content could be slightly detrimental to the process.

3-3 MAIN INDUSTRIAL REALIZATIONS and PROJECTS

3-3-1 Benilite Corp of Am.

A - Industrial realizations

. Taiwan Alkali Corp

This plant located in Kaoshiung (Taiwan) was built in two phases (1973-1975 ; 1974-1976; each phase corresponding to 15.000t/y capacity) and was completed in two years/

This plant is the first industrial realization based on the Benilite process. During the first three years the leaching solution was dumped in the sea. Presently the increase of the P.V.C production has modified the global HCl balance and a regeneration plant (W.D. process) was built because it became economically feasible.

Taiwan Alk. Corp. joined the Synthetic rutile producers by implementing the Benilite process because it had access to large quantities of "in-house" HCl.

The raw material is Indian ilmenite and it seems that large fractions of the production have been sold to Laporte (U.K.).

Taiwan Alkali Corp. is considering the possibility to build a pigment plant based on the chlorine process.

. Malaysian Titanium Corp (Malaysia)

40% Pernas (national corp.)

30% Straits (trad. comp. Singapor)

30% Empat Numbor Ekor (gambling Comp.)

This plant located in Ipoh, was completed in mid. 1976. The start up (end 1976) has been a little bit delayed by some trouble on the regeneration section.

The capacity is 60,000 t/y (exp. as TiO_2).

The planning stage of this plant was initiated in 1971, the construction began in 1974 and the plant was completed in 1976.

The raw material is the local ilmenite obtained as by-product of tin-mining the same kind of ilmenite is also available in Thailand.

The location of this plant is favored by the ilmenite availability, the capital cost, the labor cost and an important Malaysian tax advantage which is given for 5 years to the first plant of its type in any specific industry.

The acid is regenerated for economic reasons and ferric oxide is presently stockpiled.

Most of the production is sold in the US and in Japan.

As far as its future development is concerned, the company might consider expanding its S. Rutile production with the help of a partner (e.g. joint venture) and its management feels, that, given the local industrial environment, it would be too early to enter pigment production.

. Kerr Mc Gee :

The Kerr Mc Gee plant located in Mobile (USA) is presently completed (1976).

There is some doubt concerning the exact nameplate capacity of this plant. However it can be reasonably estimated at 50,000t/y (exp as S. Rutile).

Presently this plant is fed with imported ilmenite but will be fed with local ilmenite in the next future.

HCl is regenerated and Fe_2O_3 stockpiled.

Kerr-Mc Gee plans to build a chlorine plant at the same location.

As far as the economic aspects are concerned the location of such a plant in the USA does not seem optimum.

In fact, it seems that this is part of the Kerr-Mc Gee Corporate policy which is careful when dealing with the raw material situation and which emphasizes its independence for its raw materials supplies.

B - Projects

. Kerala Minerals (India)

In 1972 Kerala Minerals (state owned company) looked for the possibilities of valorization of the local ilmenite and decided to build a synthetic Rutile plant and a TiO_2 chlorine plant.

The nameplate capacities will be :

- 30.000 t/y for the S. Rutile plant
- 22.000 t/y for the pigment plant

Part of the TiCl_4 produced will be sold for Titanium production.

The completion of the entire project is planned for April 1980.

The realization is starting now, and Kerala M. plans to develop the marketing in the third world between 1977-1980.

The selection of the processes was "easy" since the only process available in 1972 for Synthetic Rutile production was the Benelite process. On the other hand, Kerala M. approached four pigment process licensors :

Du Pont and Bayer refused to sell a licence ; Laporte and Kerr Mc Gee announced that their respective processes were developed jointly in the U.K. and that Kerr Mc Gee was in charge of the commercialization of the process. Finally Kerala M. signed a global contract with the following companies :

Benelite, Kerr Mc Gee and Woodall Duckham

. Indian Rare Earth

Indian Rare Earth is starting the construction of 45.000 t/y S. Rutile plant based on the Benelite process. This plant will be located in the orissa state (India) on an ilmenite deposit which is not mined yet. Indian Rare earth consider that they will be able to sell the S. Rutile at 180 US \$/t (f.o.b.).

Indian Rare Earth has no immediate project in the pigment field but might consider it within 10 years.

. Sakai (Japan)

Sakai has decided to choose the Benelite process, 6 years ago (at this time no other process was sufficiently reliable).

Presently the total project which includes a S. Rutile (30,000 t/y) plant and a TiO_2 chloride plant is postponed due to the slow down of the pigment industry in Japan.

Sakai plans to locate his plant in Japan, it seems that it is mainly for political reasons. Presently Sakai buys ilmenite in Malaysia and in Australia.

It is worth noting that Sakai is a subsidiary of Mitsubishi Mining which is developing a S. Rutile process.

C - Long range prospects

- in the U.S.A.

A part from the Kerr Mc Gee realization, Benilite has an other contact (no precision available), but the location in the USA is not very attractive except for a general R. Material policy.

- in the Europe

Large ilmenite reserves are available in Europe in Norway, in Finland and it could be attractive to produce S. Rutile.

Benilite has many contacts with the finnish government, with Norway and with Laporte in the U.K.

The finnish situation is quite unique since their ilmenite is a by-product and the total production is limited to 150.000t/y. It is not economically feasible to produce more ilmenite since it is extracted from an underground deposit. The total production is used in Vuorikemia Oy plant (Sulfat proc.). This company is examining the possibility of using the Benilite S. process to reduce their effluent problems.

In Norway the ilmenite deposit is presently mined by National Lead.

No details concerning the Laporte project are available.

- in Australia
one contact but no precision available.

3-3-2 Dhrangadhra Chemical Works

A - Realization

The Dhrangadhra C.W. plant (loc : South of Madras) was started up in 1971, and was the first S. Rutile plant with a regular production. This production is about 20,000 t/y (S. Rutile) depending on the output of the caustic soda plant from which HCl is a by-product. This availability of HCl has led Dhrangadhra to build such a plant.

Presently the hydrochloric acid is not regenerated. Dhrangadhra C.W. has decided to build a W.D. regeneration unit which be completed in beg. 1978, thus allowing an increase of the production.

The Ilmenite is bought to Indian Rare Earth. The S. Rutile is sold on the spot market mainly in the U.S.A.

B - Project

No project except the W.D. unit construction

3-3-3 Ishihara Sangyo Kaisha

A - Realization

The I.S.K. plant located in Yokaichi was completed in March 1971 and was designed for capacity of 25,000t/y. Presently this capacity is about 42,000 t.

In 1974 the actual production was 31,500 t, 13,000 of which was sold to Japanese titanium producers and 18,500t to chloride processed TiO₂ producers in US.

Presently most of the production is used in the Ishihara S.K. chloride plant.

B - Project

I.S.K. consider that they can extend the capacity of the S. Rutile plant up to the same capacity as the TiO_2 sulfate plant (100,000 t/y) and keep using the waste acid.

Presently there is no definite project.

3-3-4 Quebec Iron Titanium

A - Realization

The Q.I.T. plant in Sorel (producing about 850.000t/y of slag - 70% TiO_2) is well known. Hence it is not necessary to go into the details except for noting that Q.I.T. does not plan to do any extension in Canada within 10 years or so and prefers to favor the Richard Bay project

B - Project

In order to extend its global capacity Q.I.T. has decided to change the location of its production in order to switch to a better Raw material that the canadian Ilmenite.

The Richard Bay (South Africa) was selected for the following reasons :

- the local ilmenite is not very rich but it is a good quality Ilmenite and it is very easy to mine. This ilmenite does not exclude the possibility of using R.B. slag in the chloride process
- local harbor facilities were already available

The capacities will be as follows :

- 400,000 t/y (slag 85% TiO_2)
- 25,000 t/y Rutile

The total investment is 350 MUS \$.

The first production of rutile is planned for mid 77.
The first production of slag is planned for mid 78.

Presently the samples which have been given to the TiO₂ producers, have been produced in a pilot in Sorel (Canada) ex-Ilmenite from South Africa.

The amount of these samples is not enough to run reliable tests which would definitely prove that this raw material is suitable for the chlorine process.

3-3-5 Western Titanium (Australia)

A - Realization

Western Titanium ran a pilot from 1968, to 1974. In mid 1974 they completed a plant having a capacity of 36,000 t/y.

This capacity will be increased up to 57,000 t/y in 1977. This increase partly is due to the switching from Capel Ilmenite to Eneabba Ilmenite.

B - Project

Western Titanium is presently having contacts with two companies in order to sell its process ; however no details are available.

3-3-6 Other projects

A - Projects

- In Australia

- Western Mining Corp. has bought the entire issued capital stock of Black Sand and plans to sell rutile and maybe to produce Synthetic Rutile at Jurien Bay.

- Westralian sand has considered the possibility of building a 100,000 t/y S. Rutile plant in a joint venture with Leonard concerning the advancement of the project Oil Co. No information

3-4 ENVIRONMENTAL IMPACT

3-4-1 Slag process

In this process Ilmenite is converted into two usable fractions, e.g. :

- slag (70% or 85% TiO_2)
- Pig. Iron

The CO obtained as by-product is burned as fuel.

Such a process can be considered as producing very few solid and gaseous wastes.

3-4-2 Upgrading processes using an acid leaching

A - leaching with HCl

Examples : Benilite Corp. of Am., Murphyores.

In this case the metals removed from the Ilmenite are obtained as chloride dissolved in water. The specific composition varies with the Ilmenite and with the process.

A typical composition of this solution (Benilite process) as follows :

- | | |
|-------------------------|-------------|
| - Iron chlorides | 20-23% (wt) |
| - other metal chlorides | 4% |
| - free HCl | 2% |
| - water | balance |

This type of solution is equivalent to pickling liquors found in the metallurgical processes and can be treated by many processes such as the Lurgi process and the Woodall Duckham process (annex p A18-A19). The by-products are Fe_2O_3 and HCl (which can be recycled) typical analysis Fe_2O_3 91-92%, TiO_2 2-2.5%, MnO 3.5%, $MgO \approx 1\%$, $Al_2O_3 \approx 1\%$, etc Murphyores inf).

With such treatment processes, the upgrading routes are pollution free.

In some cases, for example in Taiwan (already realized) and in Indian (Dhrangadhra project), the commercial price of HCl reached a level at which the treatment became economical. Initially this treatment had not been installed and we have developed an economic of such a treatment in section 2.

It is difficult to establish any superiority of either one of these two processes, but it is worth noting some key features of the two routes :

- the Woodall Duckham process deals with the chlorides in solution and has been already used many time within a synthetic Rutile plant
- the Lurgi process has never been used in this field ; it deals with the cristallized chlorides and in some cases it can reduce the energy consumption. Moreover the selective cristallization step can yield high quality oxides. A shortcoming of this process is the small CaCl_2 content acceptable for the good fluidized bed operation.

As far as the physical characteristics are concerned there is no clear cut advantage for any ferric oxide produced by either route.

B - Leaching with H_2SO_4

Example : Ishihara Sangyo Kaisha

Although the only plant using this process does not recycle the sulfuric acid (the leaching solution is used) it must not be taken for granted that there is no possibility.

Ferrous sulfate in solution could be cristallized and treated (roasting, etc) as Copperas, etc.

C - Leaching with FeCl_3

Example : Summit - Tiron

Iron is obtained as ferrous chloride. Oxidation of the solution convert a fraction of the chlorides to Iron hydroxide whereas the balance is converted to Ferric chloride which is recycled to the leaching step. About 5% of the solution is purged so as to avoid the impurities accumulation. Iron hydroxide can be dried to yield ferric oxide.

Such a process can be considered as being pollution free but no full scale realization has been done yet.

3-4-3 Upgrading process using an aeration step

Example : Western Titanium

In this process most of the Iron is remove as Fe_3O_4 and therefore can be consider as relatively free of pollution. Presently in the Western Titanium plant in Capel the Fe_3O_4 is separated as a humid cake and is dumped as such in holes. Only a very small fraction of the iron is removed in the leaching step and therefore very little ferrous sulfate is produced. Presently, in the Western Titanium plant, the leaching solution is neutralized.

3-4-4 Process using selective chlorination

Examples : chlorine technology process, Mitsubishi Metal

In such a process, Iron and other metals are removed as chlorides in the gaseous form.

After condensation this chlorides could be hydrolyzed with a Lurgi ; but in this case the by-product is HCl which in general cannot be locally used. It is the reason why the companies using this process are studying an oxidation route which would yield Cl_2 and Metal oxides as by-products ; but presently this process is still considered as not being sufficiently reliable.

3-5 LICENSING POLICY3-5-1 Benilite Corp. of Am.

As far as the number of S. Rutile plant is concerned B.C.A is undoubtedly the leader in this field ; however this position does not garanty the superiority of the B.C.A over the other upgrading processes presently available.

As Benilite Corp. of Am. is a process development company, the incentive to sell its process was clear and the commercial action for this was started very early and was very active. Five years ago it was the only company which was able to offer a licence for a commercial plant, moreover this process represented a good way to use an existing HCl excess.

After having licensed six plants in the world and granted options, Benilite has decided to be more selective in its licensing policy, except in the US.

Benilite prefers to favor the extension of the existing plant. In Europe Benilite does not want to license more than two companies.

This attitude could be considered as a "minimum-risk" policy.

3-5-2 Dhrangadhra Chemical works

This company has made many improvements in its original plant and can therefore be considered as having a good know-how ; but it must be noted that the two indian projects are based on the Benilite process.

It might be because Dhrangadhra is a chemical producer and not especially keen about selling its know-how.

3-5-3 Ishihara Sangyo Kaisha

As many producers, Ishihara S.K. did not follow a definite licensing policy immediately. Presently Ishihara S.K. is opened to consider the licensing of its S. Rutile process.

It must be noted that the present context of I.S.K. is not unique and in some cases it could allow the producer to switch the acid effluent problem to a Copperas disposal problem which is easier to solve.

3-5-4 Quebec Iron Titanium

Q.I.T is a producer which has a quasi monopoly of slag production, moreover the minimum size of a plant based on this process is such that the general strategy is completely different from the licencing policy in the S. Rutile field.

3-5-5 Western Titanium

Western Titanium is also a producer and as Ishihara S.K. did not have a definite policy immediately, moreover the process was not completely proved with respect to the product quality.

Now the process seems to be completely proved and this company is opened to :

- process licencing
- joint venture in Australia

3-5-6 Murphyores (Annex p A24)

"The Murphyores know-how for a completely engineered plant can be offered on a world-wide basis.

SECTION 4

RAW MATERIALS

SECTION 4

RAW MATERIALS

4-1 Qualities of raw materials

4-2 Mineral reserves in the World

4-3 Minerals production

4-4 Prices and market

4-1 Raw materials qualities

4-1-1 Ilmenite

We will not come back on an extensive description of the different minerals, this has been already done many times.

In the table 4-1 we have shown the compositions of the main ilmenites available.

Each ilmenite is referenced by a number (see table next page) which is used on the three following sketches.

These compositions can be examined in function of the main constraints of the sulfate, chloride, and upgrading processes, e.g : chromium, vanadium, calcium contents, oxidation degree, etc.

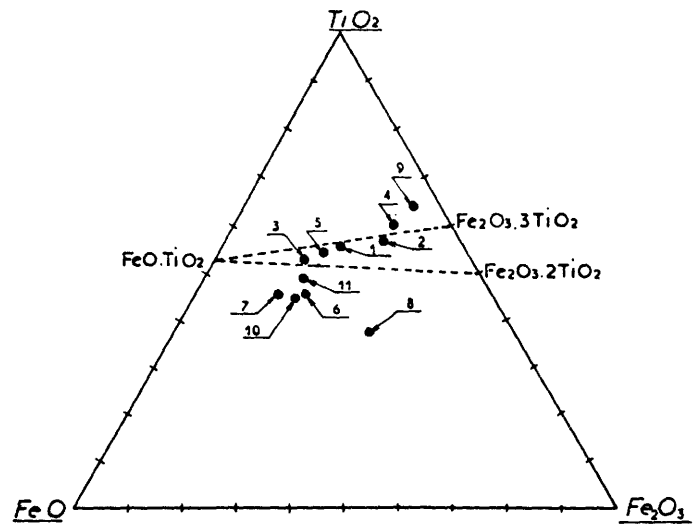
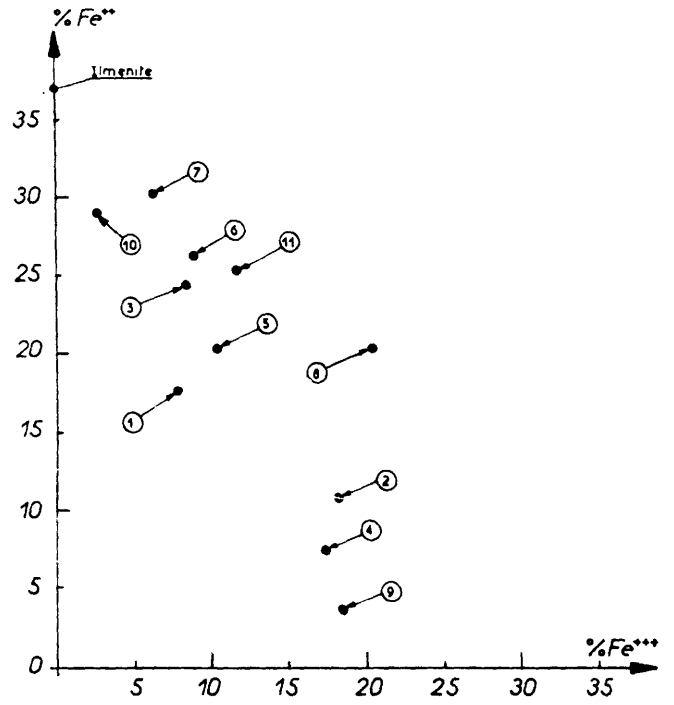
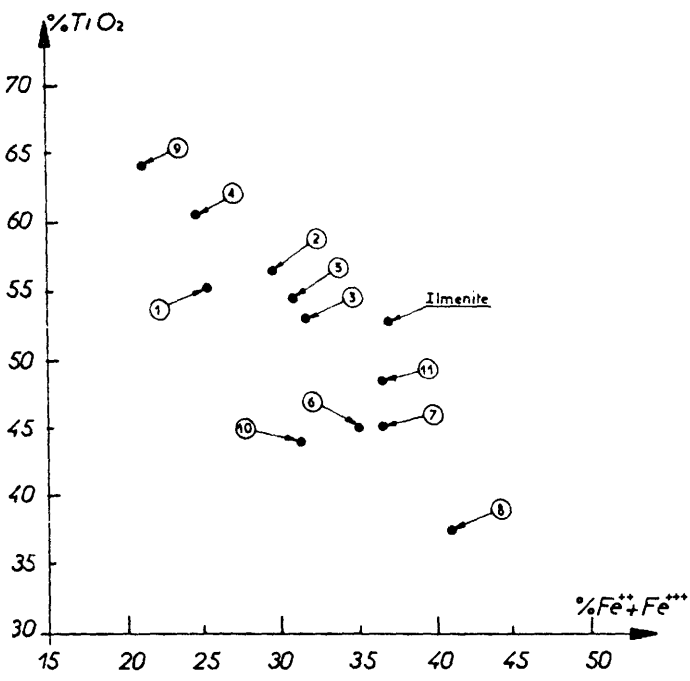
The indian ilmenite coming from Quilon is named "Q grade" whereas the "M.K grade" corresponds to ilmenite from Manavalakurichi.

TABLE 4-1

TYPICAL ANALYSES OF SOME ILMENITE CONCENTRATES

4-3

	① AUSTRALIA		③	④ INDIA		⑤	⑥ EUROPE		⑦	⑧ N.AMERICA		⑨	⑩	⑪ BRAZIL
	Western Titanium	Westralian Sand	East Coast	Quilon	M.K.	Norway	Finland	Canada Allard	USA Florida	USA N.Y.				
TiO ₂	55.4	56.0	52.9	60.3	54.3	45	45	34.3	64.1	44.4				48.3
FeO	22.5	14.0	30.8	9.7	26.0	34	39	27.5	4.7	36.7				32.4
Fe ₂ O ₃	11.1	26.0	11.9	24.8	15.5	12.5	9.3	25.2	25.6	4.4				16.6
SiO ₂	1.44	0.7		1.4	1.4	2.7	1.7	4.3	0.3	3.2				1.4
Cr ₂ O ₃	0.03	0.04	0.15	0.14	0.07	0.075	0.004	0.1	0.1	0.001				0.5
CaO		0.02	0.05	0.15	0.08	0.25	0.66	0.9	0.13	1.0				0.1
Al ₂ O ₃		0.5	0.23	1.0	1.1	0.6	1.71	3.5	1.5	0.19				0.3
V ₂ O ₅	0.13	0.2		0.26	0.20	0.16	0.27	0.27	0.13	0.24				0.06
MnO		0.5	1.77	0.40	0.40	0.25	0.75	0.16	1.35	0.35				0.6
MgO		0.2	0.46	0.65	0.85	5.0	1.36	3.10	0.35	0.8				0.1



4-1-2 Upgraded Minerals

We have shown in table 4-2 the composition of the main upgraded minerals.

It must be noted that :

- the Richard Bay slag is not yet available
- the Murphyores synthetic Rutile is not produced at an industrial scale. The composition which is shown corresponds to an ilmenite from the Australian west coast
- the slags do not contain any ferric oxide but ferrous oxide and Iron
- the Richard Bay slag contains much smaller quantities of CaO than the canadian slag and its vanadium content is the same as natural rutile.

TABLE 4-2

UPGRADED MINERALS AND SYNTHETIC RUTILE

%wt	Slag 70% (Canadian)	Slag 85% (R.Bay)	Synthetic Rut. Murphyores W.Coast	Synthetic Rut. Ishihara	Natural Rutile
TiO ₂	71	85	95.5	96.1	96.6
FeO	13.5	11 max.	-	-	-
Fe ₂ O ₃	-	-	1.2	1.7	0.35
SiO ₂	4.25	1.0- 2.5	1.0	0.5	0.35
Cr ₂ O ₃	0.25	0.3max	0.02	0.15	0.30
Al ₂ O ₃	5.0	1.5 - 3.0	0.2	0.46	0.45
V ₂ O ₅	0.55	0.6max	0.06	0.20	0.66
MnO	0.23	1.5 - 2.5	0.05	0.03	0.02
MgO	5.0	0.7 - 1.3	0.05	0.07	0.06
CaO	1.2	0.15		0.01	0.01

4-2 MINERAL RESERVES IN THE WORLD

4-2-1 Ilmenite

We have shown in table 4-3, indications concerning the main deposits of ilmenite. For each deposit we have given, the location, the raw mineral TiO_2 content, the commercial ilmenite TiO_2 content and the main mining company.

In many location the volume of the reserves does not set a limit for a future developement.

It is more a question of ilmenite quality, local context, politic.

4-2-2 Rutile

In some locations Rutile is obtained in small quantities as co-product of ilmenite (e.g. India, South Africa).

Presently Australia (East Cost) is the only location where rutile can be mined economically. In this case Zircon is co-produced and the ilmenite which has a high chromium content (not acceptable for the sulfat process), is stockpiled.

The Rutile reserves of Australia is about 5.5 M tons.

In fact this number cannot be considered as such, since the cost of mining a given deposit determines its future potential in a competitive environment.

Some other locations correspond to very big reserves and the possibility to find a new technique allowing a good cost of production could represent an increasing threat for a new synthetic rutile industry.

Brazil in Sierra Leone has got very important reserves which could potentially represent an important production of Natural rutile.

TABLE 4-3
WORLD RESERVES OF ILMENITE

The data given below are not an exhaustive evaluation of the world reserves, but are presented in order to indicate the potential capacities of the economically feasible deposits.

It must be noted that some evaluations are conservative due to the fact that producers have proved only fraction of the reserves.

COUNTRIES	AREA	Estimated Reserves M. long tons	TiO ₂ Concentr. v.s. estimat. (%weight)	TOTAL TiO ₂ content M. long tons	TiO ₂ in Concentrate	REMARKS	MAIN MINING COMPANIES (Ilmenite)
AUSTRALIA	West Coast .Capel	10	54	5.4	54	In operation	-Western Titanium 77% Consol. gold fields -Cable Sands Pty -Westralian Sands -Western Mineral Sands Pty. Ltd. (2/3 PTP and 1/3 Westralian Sands) -Allied Eneabba (75% Allied Minerals, 25% DuPont)
	.Eneabba	10	59	5.9	59	In operation (begin. 1976)	
	East Coast	Rutile Co-prod.				Not presently used because of the high chromium content	
BRAZIL	Araxa	150	10	15.0	-	Two japaneses companies showed interest for this deposit	-Rutile e Ilmenite do Brazil -Commission of Nuclear Energy -Joint venture(project) .Ishihara (Jap.) .Itoh (Jap.) .Two Brazilian Comp.
CANADA	Allard Lake	100-150	34	43	34	34% of TiO ₂ is the highest con- centration that can be reached by physical concentration	-Quebec Iron Titanium . 2/3 Kenecott Copper . 1/3 N.J.Z.Co
EGYPT	Nile Delta	15	Raw ore			-low TiO ₂ content -USSR was interes- ted in manufac- turing slag	-Egyptian Black sands (state owned)
FINLAND	Vuotijoki	20	15.6	3.2	44	Ilmenite is ob- tained as a co- product of macad- am, magnetite and pyrite and the feasibility of its recovery is therefore directly related to the mar- ket of the other products	-Rautaruuki Cy (alone) (State owned)
INDIA	-Quilon (Kerala State)	16	58	9.3	58	in operation	-Indian Rare Earth (State owned) -Kerala minerals (State owned)
	-Gopalpur (Orissa State)	20	53	10.6	53	not in operation	
MALAYSIA	Ipoh	by product from tin mining			52		-Several small companies -Boonsoong Tin Dregding Co
THAILAND							
NEW ZEALAND	-Wesport	50	Raw ore	-	-	not in operation	-Rutile and Zircon Mines
NORWAY	Tellnes	250	17	42.5	44		-Titania AS (alone) (subsidiary of N.Lead)
SOUTH AFRICA	Richard Bay	41	47	20	47	not in operation	-Cape Morgan Titan.Mine -Industrial Development Corporation (State Owned) (joint venture with QIT)
SRI LANKA		3	52	..5t			-Ceylan Minerals Sands (alone)
UNITED STATES	New Jersey	25	45	11.2	45		-American smelting and Refining Cy (A sarco) -DuPont -National Lead -Glidden Durkee -Titanium Enterprises
	Florida						
MALAGASY REP.		10	50			not in operation	

4-3 MINERALS PRODUCTION4-3-1 Prior 1975

The production of Minerals between 1965 and 1974 are shown in table 4-4 and figure 4-1.

The total quantities are converted to TiO_2 content.

For this period it can be noted that :

- the total ilmenite production has increased at an average rate of 4.6% per year
- the natural rutile production is almost stabilized since 1969
- the synthetic rutile production increases steadily

Now, if we consider more detailed information we can note that:

- the Australian production of ilmenite and rutile is no more increasing
- the Canadian production had been increasing till 1972 and has been stabilized
- the Finnish production is limited at about 160 m. T/y because Finnish ilmenite can only be supplied economically as by-product and because the local production of the main product does not increase
- the American production of ilmenite is decreasing
- for the last years the increase of production is mainly due to the increasing production of Norway, India, Sri Lanka and Malaysia.

WORLD PRODUCTION OF TITANIUM CONCENTRATES (x 1,000 long tons)

The quantities correspond to the gross weight of Minerals

WORLD PRODUCTION OF ILMENITE (x 1,000 long tons)

	(TiO ₂ %)	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
Australia	54	441	513	544	550	705	872	830	709	709	768
Brazil	48	10	13	15	18	18	-	11	4	5	5
Canada	71	487	469	538	601	669	766	774	835	855	850
Finland	44	105	116	125	138	136	-	139	150	159	152
India	59	30	30	41	58	47	-	66	72	72	77
Japan	slag	(3)	(6)	(7)	(6)	-	-	(2)	(2)	(2)	(2)
Malaysia	53	122	116	89	124	127	-	156	152	152	190
Norway	44	277	364	419	396	-	-	642	608	730	848
Portugal	52	-	-	-	-	-	-	0.9	0.7	0.5	0.5
South Africa	49	-	-	-	-	16	-	-	-	-	-
Spain	49	20	44	36	38	29	-	24	23	17	-
Sri Lanka	53	60	41	52	74	82	-	93	83	94	82
United States	av-54	866	862	835	874	831	787	620	631	713	675
TOTAL GROSS WEIGHT	-	2,418	2,568	2,694	2,871	-	-	3,355	3,267.7	3,491.2	3,647.5
TOTAL TiO ₂ CONTENT	-	1,348	1,415	1,490	1,597	-	-	1,865	1,831	1,942	2,015

WORLD PRODUCTION OF NATURAL RUTILE (x 1,000 long tons)

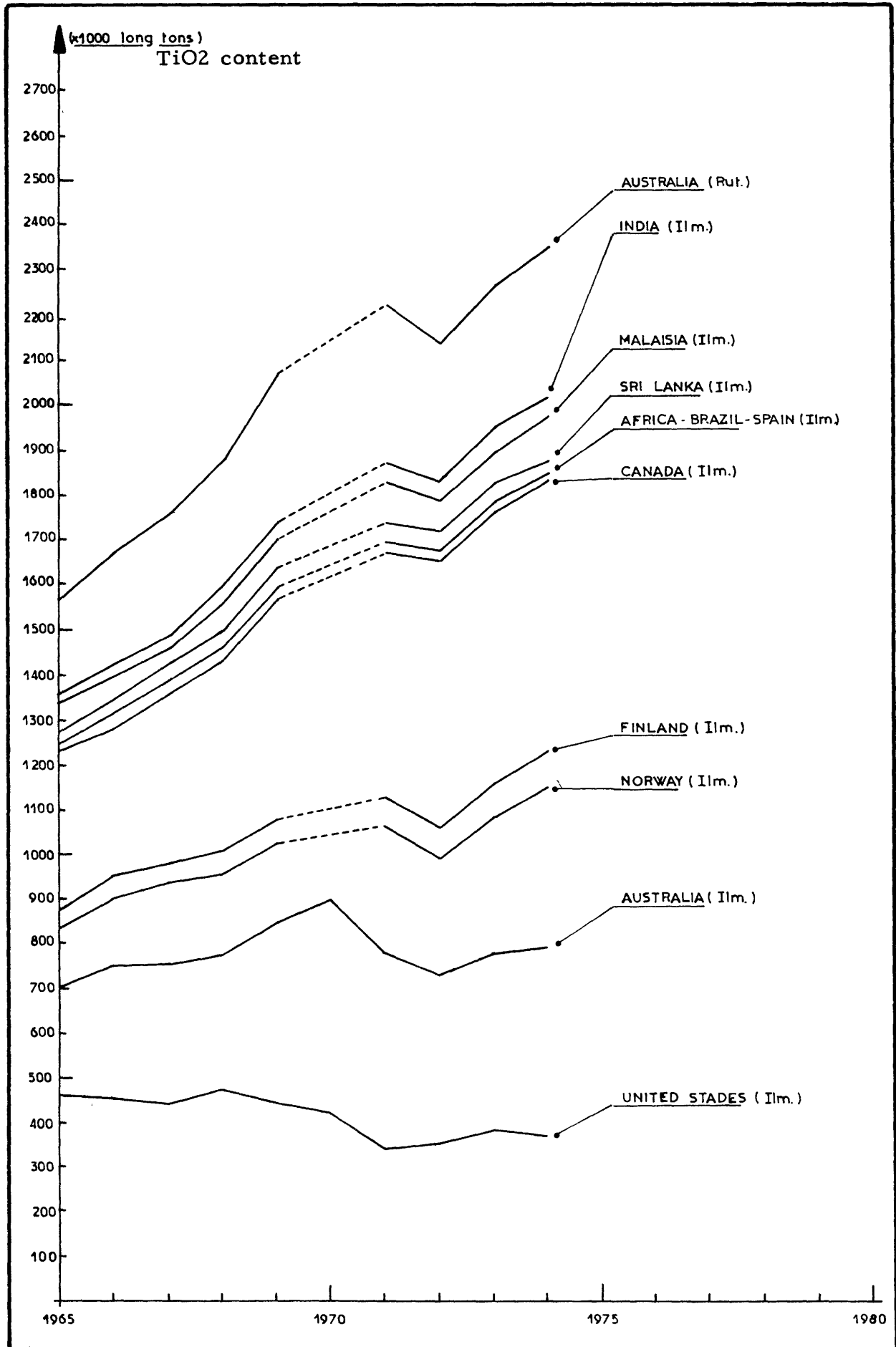
	(TiO ₂ %)	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
Australia	(96)	217	244	266	289	348	-	367	318	328	327
Brazil		0.3	0.03	0.3	0.1	0.1	-	0.1	0.45	0	0.2
India		1.3	1.8	2.5	2.6	2.5	-	2.9	3	3	3.5
Sierra Leone		1.3	1.8	2.5	2.6	2.5	-	12	-	-	-
South Africa		-	-	-	-	0.5	-	-	-	-	-
Sri Lanka		-	-	-	-	-	-	2.8	2.8	2.2	3.0
U S A		6	6	6	2	-	-	-	-	8.4	5.7
TOTAL GROSS WEIGHT		225.9	253.6	277.3	296.3	353.6	-	384.8	324.3	341.6	339.4
TOTAL TiO ₂ content		217	244	266	284	339	-	369	311	328	326

WORLD PRODUCTION OF SYNTHETIC RUTILE (x 1,000 long tons)

	(TiO ₂ %)	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
Australia	(94)	-	-	-	-	-	-	-	8	8	18
India		-	-	-	-	-	-	-	20	20	20
Japan		-	-	-	-	-	-	-	25	25	31.5
Taiwan		-	-	-	-	-	-	-	-	-	(12)
TOTAL GROSS WEIGHT		-	-	-	-	-	-	-	53	53	81.5
TOTAL TiO ₂ content		-	-	-	-	-	-	-	50	50	77

WORLD PRODUCTION OF TITANIUM MINERALS

Cumulative Diagramm



4-3-2 Tendency

The total production of minerals was 1,565 m. tons in 1965 and 2,341 m. tons in 1974, e.g. an average growth rate of 4.6% which logically should correspond to the average growth rate of the TiO_2 pigment industry.

The production of upgraded minerals are not taken into account in this data since their TiO_2 contents are already included in the ilmenite production figures.

If we consider the same average growth rate till 1980, and an average growth rate of 4% between 1980 and 1985 the total production (exp.in TiO_2 cont.) will be

3,066 m. tons in 1980

3,730 m. tons in 1985

e.g. an increase of

725 m. tons between 1974-1980

664 m. tons between 1980-1985

This figures are referred to the TiO_2 content. Such an increase can be met by slag, synthetic rutile, rutile and ilmenite. Moreover a decrease of the market of one of these minerals can lead to a more important increase of an other mineral

e.g. If the Richard Bay slag were to be used in the chloride process, this would initiate a steep competition with the other rich raw materials such as S. Rutile and N. Rutile. This competition would then lead to a stabilization of the price at a relatively low level (may be 180 UC/t ?). With such a price, some natural rutile mining could become uneconomic ; this would lead to their shut down and to a subsequent extension of the potential market for upgraded minerals.

It must be noted that this is one scenario among many others.

Presently the market for rutile is limited and important new capacities would lead to a quick price decrease. With the extension of the chloride process the overall Rutile market would become more important ;

This would make some large scale Rutile mining prospects economically feasible.

This new natural rutile mining might be able to compete with synthetic rutile or other minerals.

We have discussed these aspects in an other chapter economics figures (section2).

We will just keep in mind that, between 1974-1980, the growth of the TiO_2 demand will be around 725 m. tons.

It can be noticed that after 1974 :

- Indian has increased its production capacity by 110 m. tons/y (Ilmenite)
- Sri Lanka has also increased its production capacity by 100 m. tons/y (Ilmenite)
- South Africa plans to produce 400 m. t/y of 85% TiO_2 slag
- Synthetic rutile production has increased by 160 m. t/y (a part of this increase is already included in the ilmenite production increase)
- Synthetic rutile projects already planned for 1980 have a global capacity of 120 m. t/y, may be 200 m. t/y (100 m. t/y project is doubtful).

The total of these extensions is 720 m. t/y (expressed as TiO_2), (820 m. t/y with the 100 m. t/y project).

Apparently the supply and demand of mineral seem to be balanced. In fact the distribution of this raw materials is uncertain and in some cases this might lead to a substitution of some type of minerals by others.

4-4 PRICES AND MARKET4-4-1 PricesA - Ilmenite

Ilmenite price is very stable because of its wide availability and the numerous deposits. And like many minerals the freight cost is a very important parameter of its market.

- Australian ilmenite

1974	- 16-19 US\$/t f.o.b
May 1975	- 16-20 US\$/t f.o.b

- Indian ilmenite

1974	- 15-16.5 US\$/t f.o.b
------	------------------------

- Malayan ilmenite

1974	- 16-19 US\$/t f.o.b
------	----------------------

- freight cost example :

India-Taiwan	- 10-11 US\$/t
Australia-Taiwan	- 18-19 US\$/t

- American ilmenite

(domestic market)	- 38-55 US\$/t
-------------------	----------------

This price is possible because of the freight advantage of such an ilmenite.

B - Rutile

The rutile is not stable and some spot prices was extremely high.

1969	- Av. price	145 US/t
1979		175 " "
1971		185 " "
1972		175 " "
1975		210-230 Aus\$ /t f.o.b (290-320 US\$/t)

As example of the hectic character of the rutile price we have listed the successive spot prices of the year 1974.

1974 - January 1st	175-185	US \$/t
January 31	181-190	"
March 12	206-225	"
April 15	219-250	"
May 14	225-262	"
May 3	250-300	"
July 9	350-400	"
October 4	362-412	"

C - Synthetic rutile

Synthetic rutile production was small until 1976 and did not upset the general rutile market. Many times, synthetic rutile was sold at spot prices which were lower than the price of natural rutile at the same time.

e.g. quotations of the US Bureau of mines importation statistics dealing with rutile :

Australian : 185,091 metric tons - Value 33.628 mUS\$

e.g. an average price of 182 US \$/t

Japan 23,982 metric tons value 2,713 m. US \$

e.g. an average price of 113 US \$/t

It is possible to think that in this statistic most of the rutile imported from Japan is synthetic rutile produced by I.S.K. (before the start up of its own chloride process).

Other information from the US Bureau of Mines based on declared shipment values indicate a 155US\$/t, 260US\$/t price range (1974). Note that these prices may be spot prices for small shipments.

D - Canadian Slag

Canadian slag price rise has been steep since 1972.

aver. price	1972	50U\$/t	(f.o.b)
	1974	60U\$/t	f.o.b Sorel
May	1975	75U\$/t	f.o.b. Sorel
End	1976	102U\$/t	f.o.b. Sorel

E - Richard Bay Slag

The forecasted sale price of R.Bay slag is around 150U\$/t f.o.b. South Africa. This price is a 1978 price.

Published information indicates that five Japanese companies will buy R.B. slag at 174U\$/t (c.i.f ?).

4-4-2 Market

A - Introduction

Many kinds of ilmenite (adequate for the sulfate process) are largely available, and can be produced cheaply ; therefore the sale price is very low.

In many locations the freight cost is very high as compared to the sale price and is a very important factor of the ilmenite market.

For example the freight cost between India and Taiwan is 10-11 US\$/t whereas it is 18-19 US\$/t between Australia and Taiwan, such a difference can hardly be transferred on the ilmenite sales price.

An other selection factor can be the internal cost of production e.g a producer having sulfuric acid or chlorine will be less sensitive to the Iron content (without treatment consideration).

In some cases, financial relations with mineral producers can also be a selection factor.

An other factor which could upset the mineral market is the non pigment producers e.g. titanium metal and welding-rod coating manufacturers.

In fact this factor is limited and deals only with rutile. The main effect is on some rutile spot prices which can be very high and completely incompatible with an economical pigment production.

B - Main fluxes of Minerals

It is difficult to have a precise view of all the fluxes of Minerals between countries and some published information are difficult to crosscheck.

A detailed analysis of these fluxes is outside the scope of such a study. It is also quite difficult to understand the reasons of certain exchanges. For example, in 1974 the US minerals exports (US. Bur. of Mines) were 27.500 tons ; they were broken down as follows :

- Brazil
- Lat Am.
- Japan
- Philippines
- Far East countries
- W. Europe
- Canada

Moreover there is an evolution of these fluxes, but up-to-date information were not available. Nevertheless it is possible to indicate a typical distribution of the exports :

CONSUMPTIONS AND EXPORTS FROM MINERAL PRODUCING COUNTRIES

(Numbers quoted in parentheses are rough estimates of the corresponding 1974 consumption or exports)

AUSTRALIA

- domestic consumption (90 m. tons)
- exports
 - . Europe - mainly France (170m. ton) or UK (230m. tons)
 - . Japan (170m. tons)
 - . U.S.A. (60 m.tons)

Total of domestic consumption and exports : 760m.tons
 Australian production : 768 m. tons

CANADA (Slag)

- domestic consumption (80 m tons)
- exports
 - . U.S.A. (220 m.tons)
 - . Europe (300-350 m.tons)
 - . Japan (?)

FINLAND

- domestic consumption since 1976 Finnish ilmenite is completely used for domestic consumption

NORWAY

- domestic consumption (50 m.tons)
- exports
 - . Europe mainly Germany Italy, a few to Spain Finland and East European countries (?)

INDIA

- domestic consumption (plus future S. Rutile industry)
- exports
 - . Japan
 - . Taiwan

SRI LANKA

- domestic consumption : none
- exports
 - . Japan

UNITED STATES

- domestic consumption
- exports (30m.t)

SECTION 5

EFFLUENTS TREATMENTS

SECTION 5

EFFLUENTS TREATMENTS

5-1 Introduction

5-2 Inert Compounds

5-3 Solid salts

5-4 Sulfuric acid wastes with salts in solution

5-5 Iron oxide

5-6 Iron

5-7 Gas

5-8 Environmental pressures

5-1 INTRODUCTION

It is not within the scope of the present study to deal with the different treatments. However it is impossible to evaluate the future of the raw materials without considering at least the main features of the possible treatments or the by-products uses.

We have shown in table 5-1 the main categories of effluents produced by the pigment or upgrading processes. These effluents are gathered according to their physical composition and the corresponding treatment.

In each category we have detailed the specific effluent produced by the pigment processes or the upgrading processes. We have shown some possible treatments ; the by-products and the existing realizations.

It must be noted that the list of possible treatments and applications is not exhaustive. Moreover for each type of treatment, some particular processes may exist.

In this section we will comment the main characteristics of this table.

It must be noted that there are some detailed treatment descriptions in the annex from page A2 to A22, from page A31 to A32.

It must be noted that some rough indications concerning the amount of effluents and by products are given in section 1.

TREATMENTS					
Compound categories	Description	Origin	Possible treatments	By products	Examples of application and realization
Inert	SiO ₂ , TiO ₂ Al ₂ O ₃	Sulfat process	stockpiling Dumping		Thann et Mulhouse(Thann) Tioxide (calais) Kronos Titan (Nordenham)
Compound	ZrO ₂ , MnCl ₂ MgCl ₂ , CaCl ₂	Chlorine process	stockpiling Dumping		
Salts not in solution	FeSO ₄ , 7H ₂ O MgSO ₄	Sulfat process	Dumping		Thann et Mulhouse(Le Ha)
			stockpiling		Montedison (Scarlino)
			Drying	FeSO ₄ , 15H ₂ O	Fuji Titanium(Japan)
			Drying, Roasting	Fe ₂ O ₃ , SO ₂	Montedison(spinetta) Japanese produc.
	solid neutralization	FeSO ₄ , CaSO ₄	Japanese TiO producers		
	oxvdation neutralization	Fe ₂ SO ₃ + CaSO ₄	no realization		
	-FeCl ₃ , FeCl ₂ AlCl ₃	Chlorine process	complete transf. FeCl ₃	FeCl ₃	Du Pont* pilot: Edge moor
			oxydation	Fe ₂ O ₃ + Cl ₂	Du Pont** (pilot: N Johnson-vil)
			regeneration	Fe ₂ O ₃ + HCl	no realization
	-FeCl ₃ , FeCl ₂	Upgrading process (select. chlor.)	oxydation	Fe ₂ O ₃ + Cl ₂	Mitsubishi Metal mining (Japan)
regeneration	Fe ₂ O ₃ + HCl	Lurgi process			
Salts in solution plus acid	H ₂ SO ₄ (between 10-20% wt) FeSO ₄ (between 8-15% wt) + metal sulfats	sulfat process	Dumping		most of the Europ. produc. and Canada, Australia produc.
			Neutralization, dumping		Montedison(Scarlino)
			Complete neutralization	Fe(OH) ₂ CaSO ₄	American Cyanamid(Savannah)
				Fe(OH) ₂ NH ₄ SO ₄	Thann et Mulhouse(Thann)
				Na ₂ SO ₄	Some Japanese producers
			concentration up to 62%	H ₂ SO ₄ 62%	Some japanese producers (one in Poland)
	concentration up to 90%	H ₂ SO ₄ 96%	Bayer		
	Concentration and roasting		no realization		
	H ₂ SO ₄ between 1-3% + FeSO ₄ (very low)	Sulfat process	Dumping		most of the Europ. produ.
	Neutralization	Fe(OH) ₂ Ca SO ₄	American Cyanamid (Savannah)		
FeCl ₂ 23% FeCl ₃ 3% + misc	Upgrading process	Dumping		Dumping is now abandoned for economic reasons	
		Regeneration	Fe ₂ O ₃ , HCl	most of the synth rutil producers	
FeSO ₄ about 300 g/l + misc	Upgrading process	Dumping			
		Neutralization (NH ₃)	Fe(OH) ₂ , NH ₄ SO ₄	Ishihara S. K. (Japan)	
		Cristallization Filtrat	FeSO ₄ , 7H ₂ O		
Ferric oxide	Upgrading process	stockpiling			
		possible use in blast furnace	Fe	most of the synthetic rutil producers W. Titanium, Taiwan alk-Malays the small quantities available and the low economic incentive are mainly responsible of the low use of this by-product	
Iron		slag process	Desulphurization	Pig Iron	Quebec Iron Titanium (Canada)
gas	SO ₂	sulfat process	absorption scrubbing		most of the TiO ₂ producers
	CO HCl Si Cl ₄	chlorine process	scrubbed, flared		
	CO	slag process	used as fuel		Quebec Iron Titanium (Canada)
	HCl	Upgrading process	Scrubbing		

*: Presently : Deep well injection

** : Presently : Dumping (Sea)

5-2 INERT COMPOUNDS

We will not give any more comments about this type of effluent since their quantities and their inert character are such that the environmental and economic impacts are very small.

5-3 SOLID SALTS5-3-1 Copperas (Annex p A 4-5-6-7-8)

Copperas can be produced by the sulfate process fed with ilmenite or by upgrading processes using sulfuric acid as leaching agent.

Many copperas treatment processes have been already proposed. Some of them have been implemented on an industrial scale.

At a given time and in a given industrial context, the roasting of copperas was considered as economic (e.g. B.T.P. in UK grimsby - 1959).

Economic calculations based on the drying and roasting processes integrated with a sulfuric acid plant have shown that an extra cost of about 55 UC/t TiO_2 is added by the Cooperas treatment of a TiO_2 sulfate plant fed with Norwegian ilmenite.

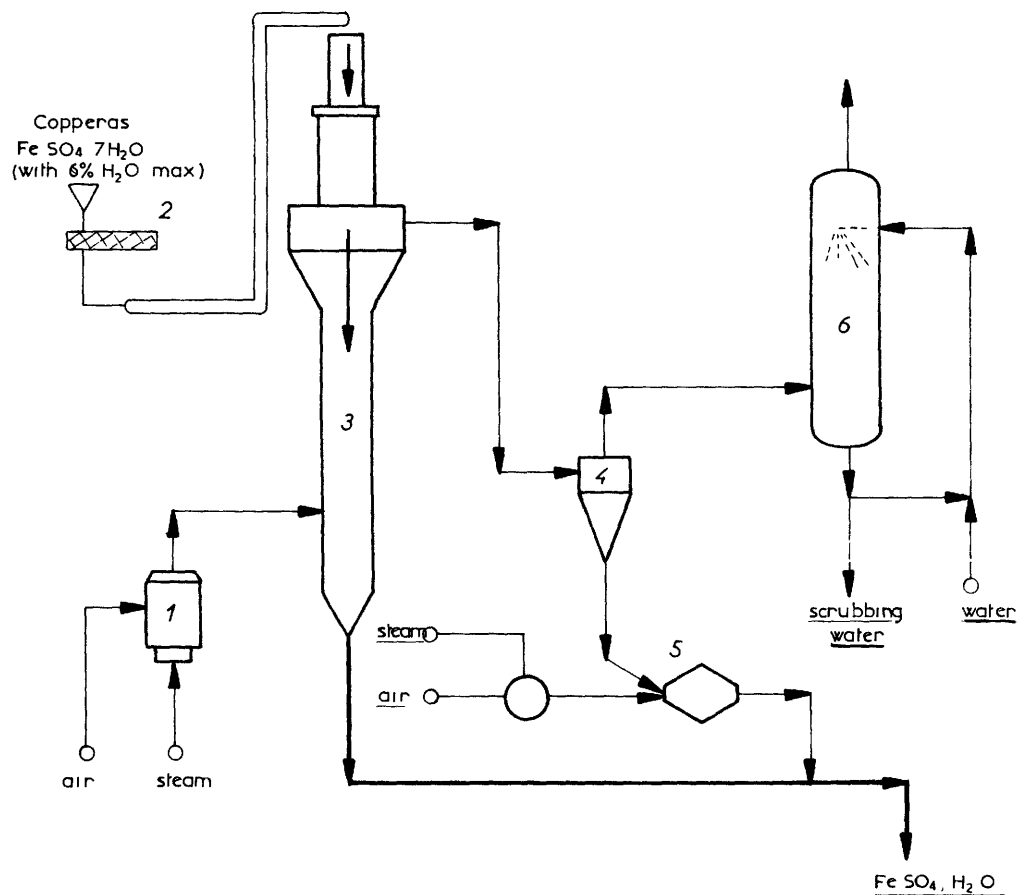
This extracost can be considered as a reasonable figure defining the upper limit of its range.

Some applications or some direct sales, may minimize this extra cost.

For example it can be noted that, in the US, the demand forecast for ferrous sulfate is 285,000 tons for 1976 and 330,000 tons for 1980. The main uses of ferrous sulfate are as follows :

- iron oxide pigments and salts	80%
- fertilizer acid stockfeed	8%
- water treatment	5%
- catalyst component	3%
- miscellaneous	3%

LURGI COPPERAS DEHYDRATION PROCESS



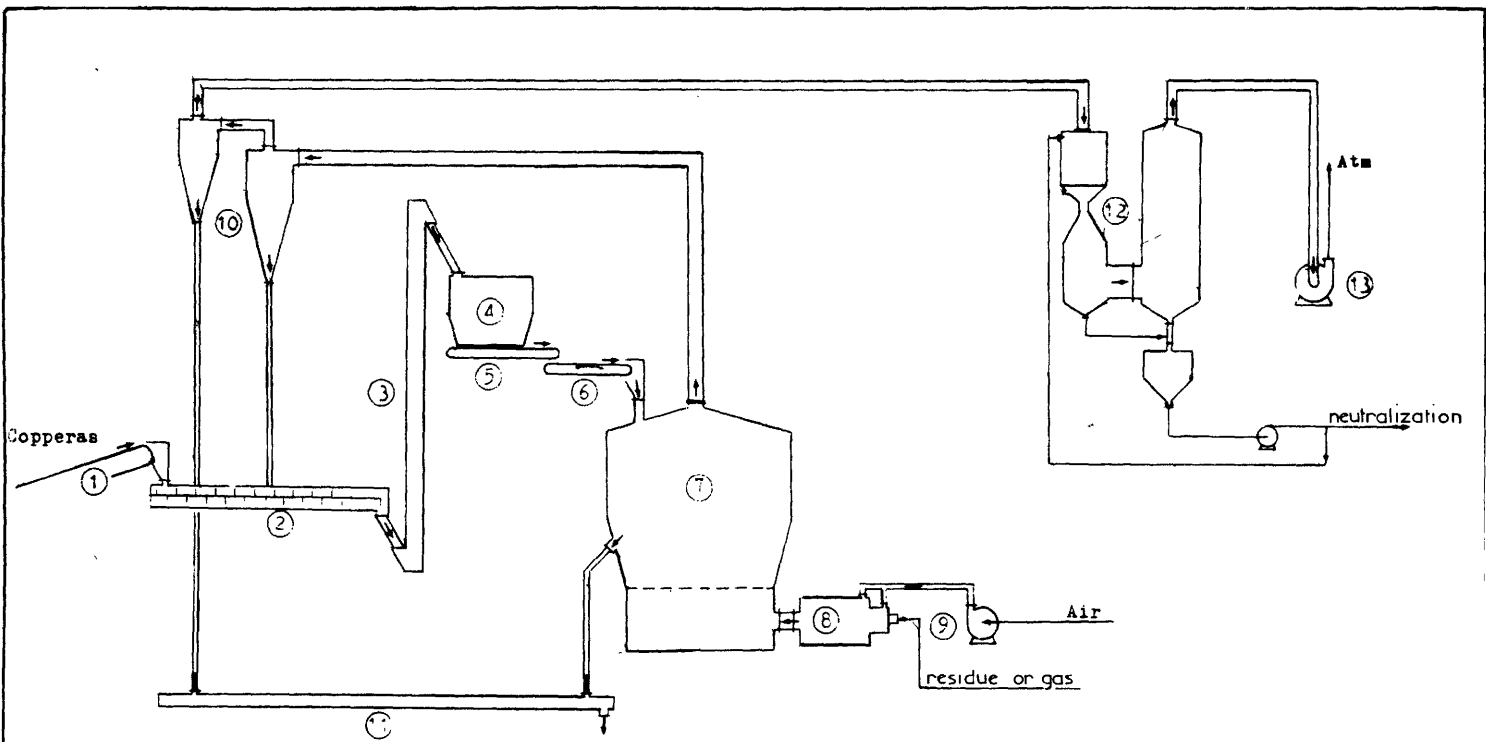
COPPERAS DRYING IN AN HOT AIR STREAM

Main features

Consumption Electricity : 100 Kwh/t Copperas
 Fuel 52 kg/t Copperas

Investments Capacity 6t/h (Copperas) Inv. 0.7 MUC/48,000 t/y
 Capacity 40t/h (Copperas) Inv. 1.8 MUC /320,000 t/y

Realization Italy - Company Montedison in Spinetta
 Yugoslavia - Cinkarna in Celje



- | | |
|----------------------|---------------------|
| 1 Conveyor | 8 Hot air generator |
| 2 Blender | 9 Fan |
| 3 Elevator | 10 Cyclones |
| 4 Feed hopper | 11 Conveyor |
| 5 Unloading conveyor | 12 Gas scrubber |
| 6 Weigh belt | 13 Vacuum pump |
| 7 Fluosolids Furnace | |

COPPERAS DEHYDRATION



DORR-OLIVER N.V.
AMSTERDAM - HOLLAND

COPPERAS DEHYDRATION

Typical unit (8 000h/y)

Investment Capacity : 50 t/h Copperas 1.5 MUC/400,000 t/y

Consumption Electricity : 55 Kwh/t copperas

Fuel : 35 kg/t Copperas

5-3-2 Iron chlorides (see Annex p A19-A21-A22)

The uses or treatment possibilities of the Iron chlorides could be a very important factor in the evolution of the future chloride process raw materials.

Iron chlorides are the main effluents of a TiO_2 chloride process fed with low grade raw material and its chlorine content has important consequences on the pigment cost of production.

Iron chlorides are the main effluent of a TiO_2 chloride process fed with low grade raw materials and even now the price of the chlorine contained in this effluent has consequences on the cost of production ; in the future, environmental impact could increase the total cost of production.

In section 2 we have done some economic calculations for a TiO_2 chloride process fed with ilmenite, but without treatment. We have also made calculations in order to evaluate the cost of chlorine regeneration by the processes presently available.

The total cost of chlorine regeneration is 160 UC/t Cl_2 (return included), this extra cost must be compared to the chlorine and the raw minerals prices. This analysis has been presented in section 2.

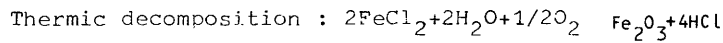
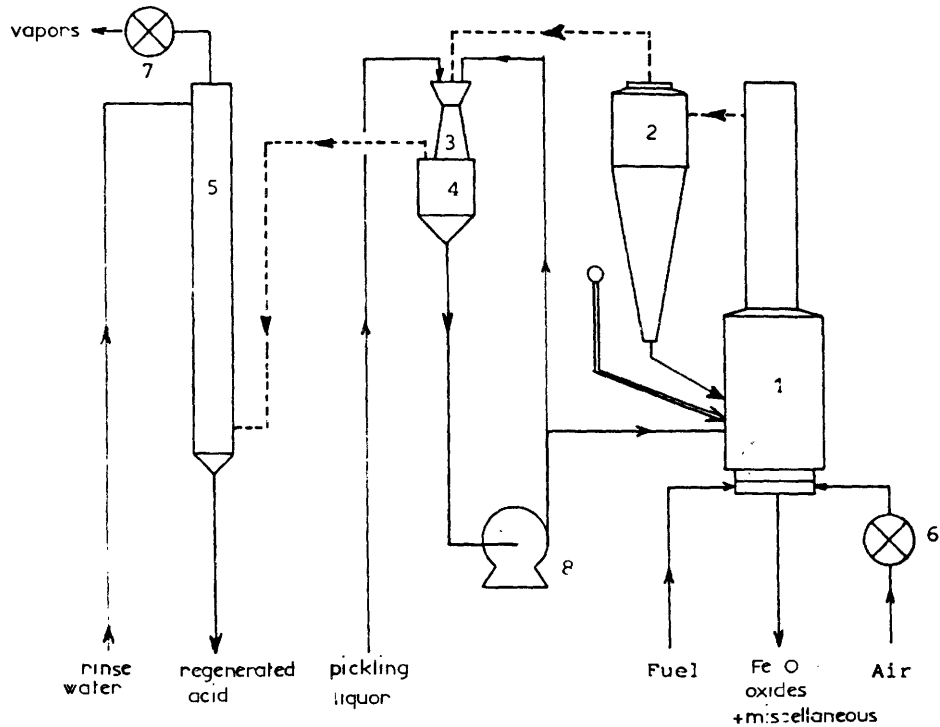
It must be noted that many companies are studying the iron chloride treatment, however no economic figures are available. The main routes presently analyzed are follows :

- direct oxidation (DuPont, Bureau of Mines
Mitsubishi, Chlorine technology)
- use of iron chlorides in water treatment
(Du Pont)
- use of iron chlorides in pigment production
(Indian laboratory)

When the iron chlorides are produced directly from HCl the complete cycle only requires a hydrolysis step ; Moreover HCl is valued at its chlorine content then the treatment becomes economically feasible.

LURGI PROCESS

PICKLING LIQUORS REGENERATION
(OR TREATMENT OF METALLIC CHLORIDES)



- 1 - FLUIDIZED BED REACTOR
- 2 - CYCLONES
- 3 - VENTURI SCRUBBER
- 4 - SEPARATOR
- 5 - ABSORBER
- 6 - BLOWER
- 7 - FAN
- 8 - PUMP

Typical unit : 8,000 h/y production HCl (Azeotropic) : 31,000t/y (100%)
Ferric oxide 28,000 t/y

Consumptions Fuel 0,75 t/h
Electricity : 1,155 Kw/h

Investment : Ferric oxid production : 5,440 t/y Inv. 1 MUC
8,800 t/y Inv. 1.2 MUC
35,200 t/y Inv. 1.8 MUC

5-4 SULFURIC ACID WASTES WITH SALTS IN SOLUTION

5-4-1 Sulfuric acid wastes (concentration between 12%-20%) with salts in solution

The main source of this kind of effluents is the hydrolysis step in the sulfate process and therefore the sulfuric acid concentration is determined by the process itself (below 25%). The amount of salts in solution can vary widely depending of the raw material (see section 1 chapter 1-1-3)

The disposal, the possible uses and the possible treatment of this effluent has been extensively surveyed.

We comment only some specific practises.

Germany

Co Bayer, Loe Uerdingen (Ref 1.2.1) Waste acid is concentrated by submerged combustion and Plinke process. Salts are roasted. The Bayer plant context is very important and allow to use the sulfuric acid in many way. It must be noted that Bayer has some trouble in regard of maintenance and air pollution.

France

Co Thann et Mulhouse - Loc Thann (Ref 3.1.1)

The plant is located very far from any disposal area. All the effluent are neutralized and the products of neutralization are stockpiled. It must be noted that this plant is very old and completely amortized, moreover its capacity is very small compared to the Havre plant. Thann is the headquarter of this company.

Italy

Co Montedison Loc. Scarlino (Ref 5.1.2)

Waste acid are neutralized and the neutralized products are dumped (see Annex 9 A9-28/A-9-29).

Poland

Waste acid is supposed to be concentrated and sold to a fertilizer plant.

U.S.

Co. American Cyanamid Loc. Savannah

Waste acid are completely neutralized. Presently the product of neutralization are stockpiled. In US this plant is the first to achieve a complete treatment which will correspond to the best available technique (B.A.T.).

Co. Glidden Durkee Loc. Baltimore

A part of strong acid is regenerated, the other part is neutralized. It seems that this plant will be able to achieve a complete treatment in November 1977.

Japan

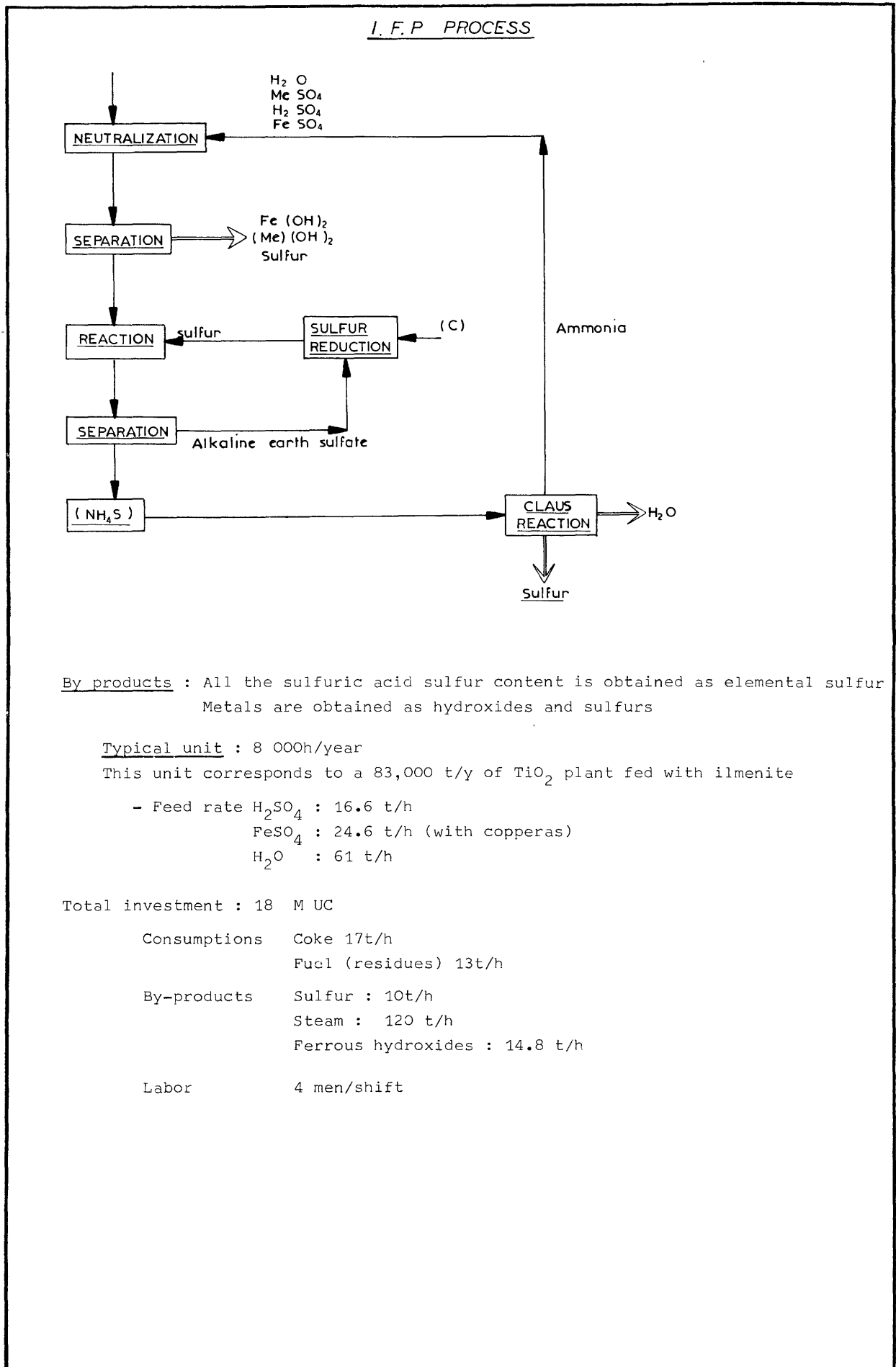
Each plants have treatment equipments.

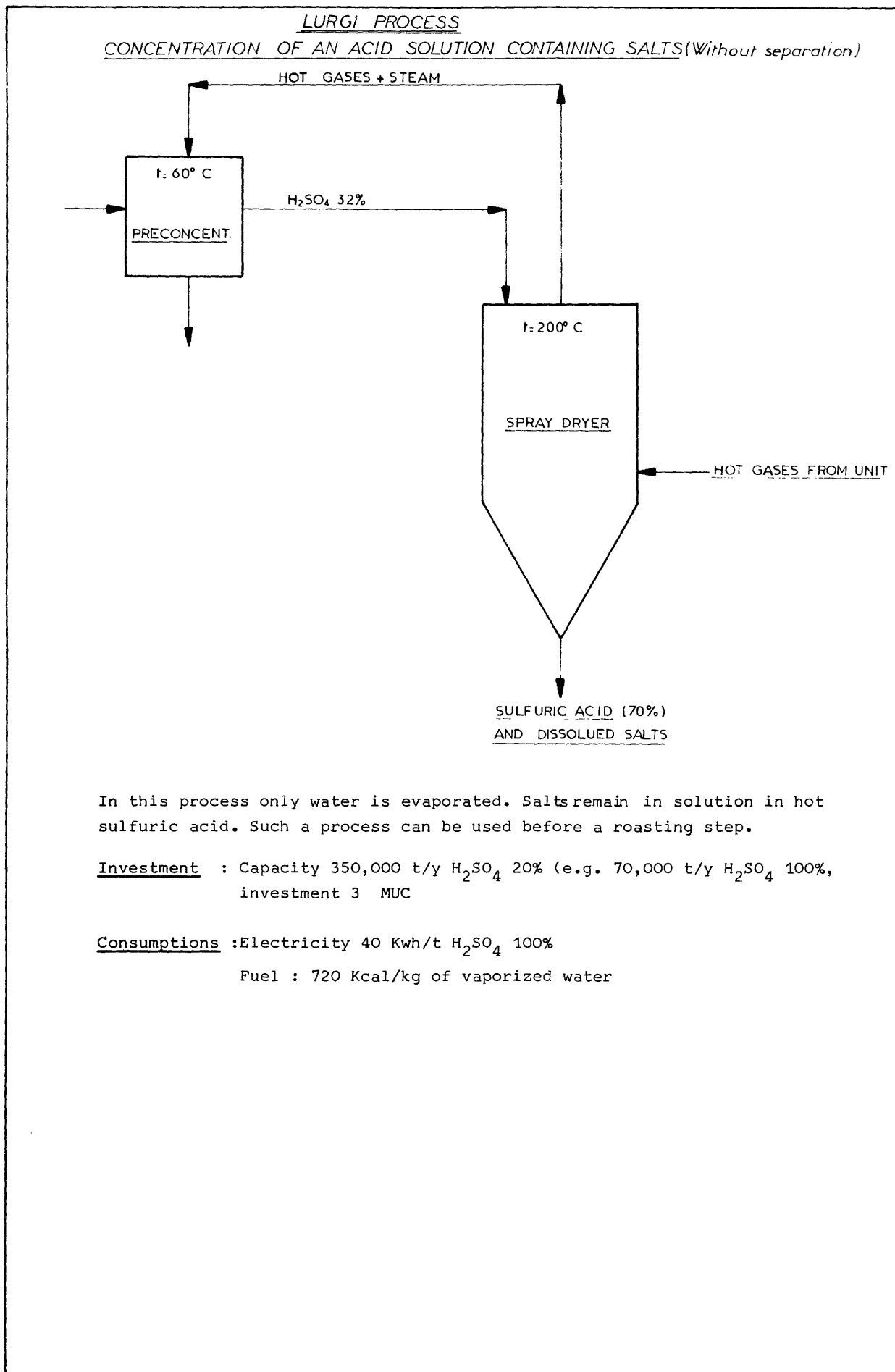
The main categories are

- complete neutralization and stockpiling (20.1.1.)
- production of ammonium sulfate
(20.2.1) (20.3.1) (20.5.1)

The Sakai company estimates at 108 UC/t the Ammonium sulfate cost of production and this company sells it at 50 UC/t, and so, as 3 tons of ammonium sulfate are produced /1ton of TiO_2 pigment the total cost of treatment can be estimated at 150 UC/t TiO_2 pigment.

- Sodium sulfate production (Ref 20-4-1)
- sulfuric acid concentration (Ref 20-6-1)(Ref 20-7-1).





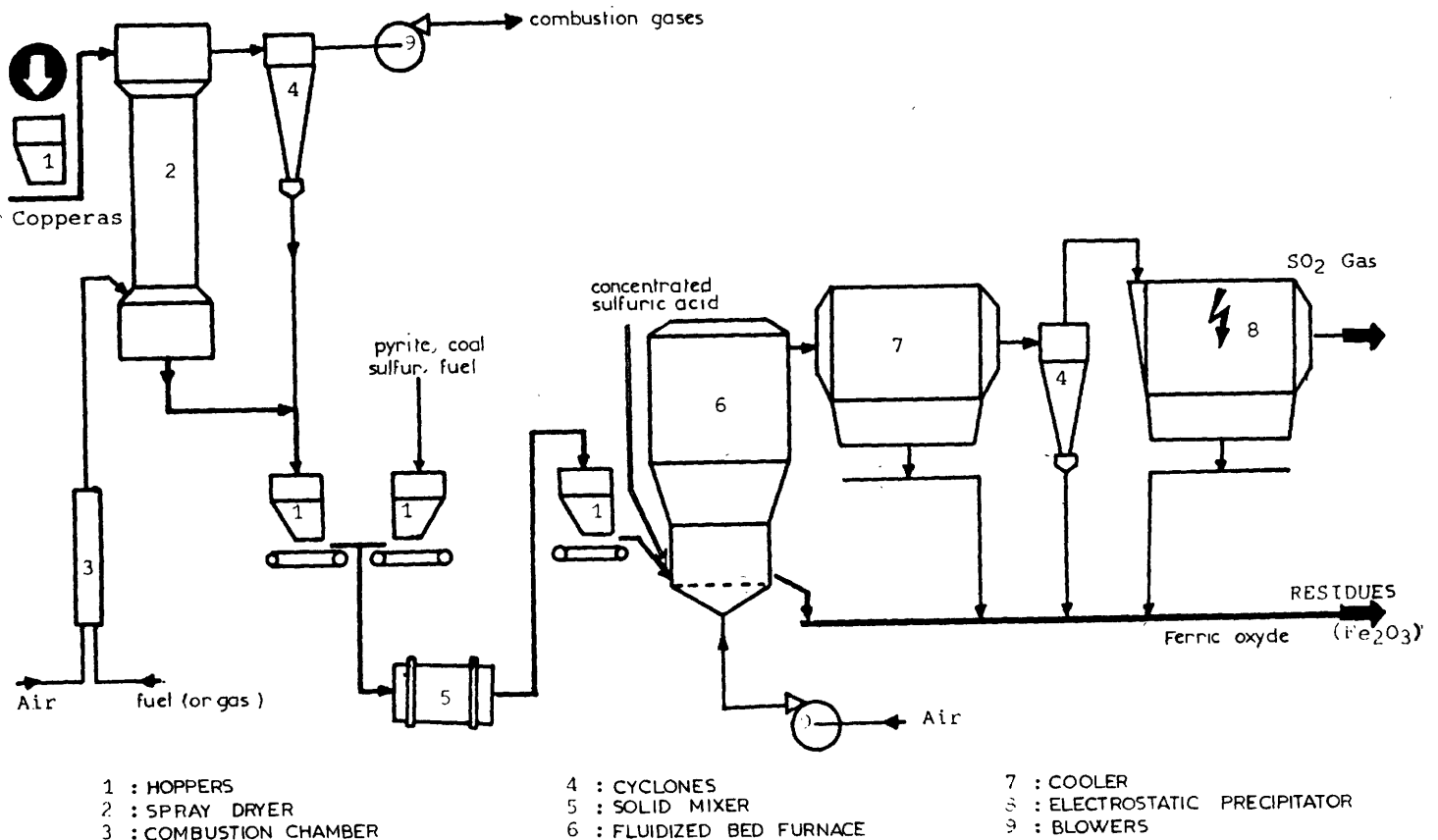
In this process only water is evaporated. Salts remain in solution in hot sulfuric acid. Such a process can be used before a roasting step.

Investment : Capacity 350,000 t/y H_2SO_4 20% (e.g. 70,000 t/y H_2SO_4 100%, investment 3 MUC

Consumptions : Electricity 40 Kwh/t H_2SO_4 100%

Fuel : 720 Kcal/kg of vaporized water

LURGI PROCESS
COMPLETE COPPERAS TREATMENT
 (With SO₂ and Fe₂O₃ production)



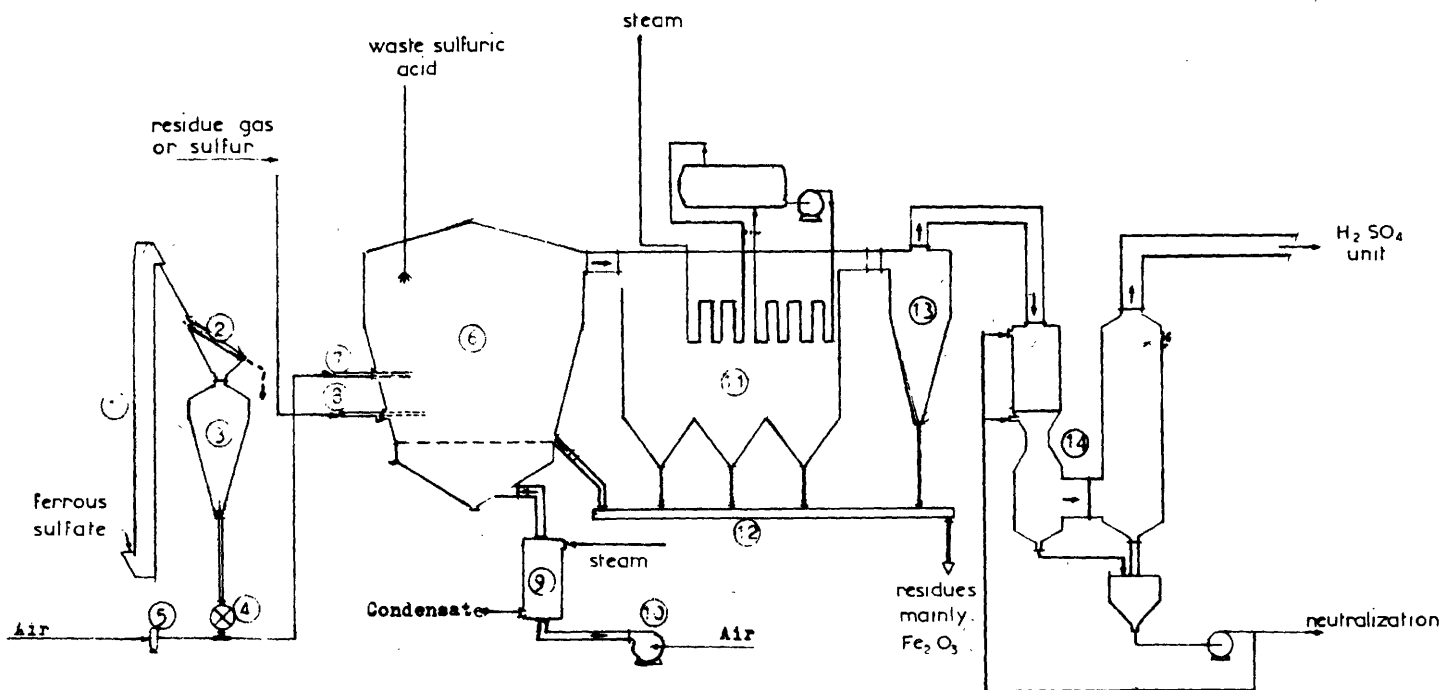
This unit included drying of Copperas, roasting of Copperas and waste sulfuric acid, gas purification, H₂SO₄ production.

Investment 28,490 - 28,280 UC/t day of H₂SO₄ 100%
 (size 300-500 t/day of 100% H₂SO₄)

Consumption Fuel - 1,00 Kcal/kg ferrous sulfate monhydrate to be roasted
 - 2,500 Kcal/kg sulfuric acid 100% to be roasted

Electricity : 30-40 Kwh/t FeSO₄

FERROUS SULFATE MONOHYDRATE ROASTING



- | | |
|----------------------|----------------------|
| 1 Elevator | 8 Fuel nozzle |
| 2 Vibrating screen | 9 Air heater |
| 3 Feed hopper | 10 Fan |
| 4 Rotary feeder | 11 Waste heat boiler |
| 5 Blower | 12 Conveyor |
| 6 Fluosolids furnace | 13 Cyclone |
| 7 Feed nozzle | 14 Gas scrubber |

FERROUS SULFATE MONOHYDRATE ROASTING



SULFURIC ACID AND COPPERAS ROASTING

Typical unit for Copperas roasting (8.000 t/y)

Investment : Capacity : 600 t/y Copperas (anhyd) 3.9 MUC

Consumptions : Fuel : 100 kg/t copperas (a hyd)

Electricity : 35 Kwh/t Copperas (anhyd.)

Realization : Italy - company : Montedison in Spinetta

5-4-2 Sulfuric acid wastes (concentration below 5%)

This type of effluent comes from the TiO_2 sulfate process or from the scrubbing water of the TiO_2 chloride process (and of the upgrading process).

In this case the water content is such that no thermic treatment can be considered.

The best way is to reduce as much as possible the acid and salts content of this stream in the main process.

E.g. Use of surface condenser instead of contact condenser, use of filter instead of decanter

Then neutralization is probably the only treatment which can be considered without too many expenses.

5-4-3 Ferrous chlorides concentration above 20% with a low hydrochloric acid concentration

This type of effluent has been already examined in the section 3 chapter 3-4 (p. 3.29-3.30).

The economic of the Woodall Duckham process has been developed in the section 2.

5-4-4 Ferrous sulfate concentration above 20% with a low sulfuric acid concentration

This type of effluent can be produced by an upgrading process using sulfuric acid as leaching agent (e.g. Ishihara S.K. process).

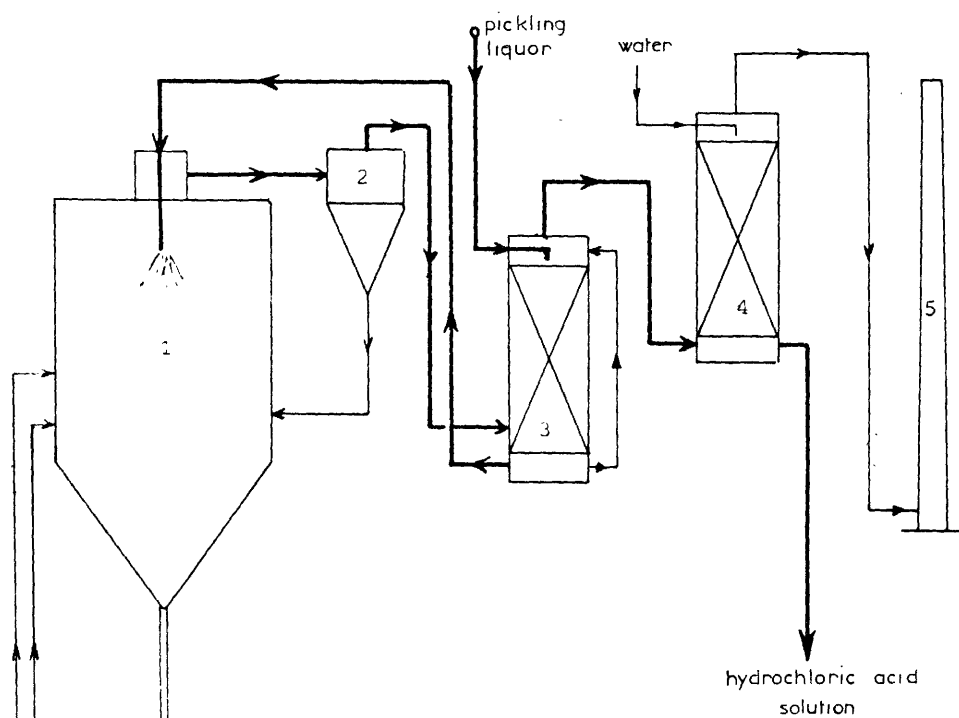
Only one producer is using this way (ISK in Japan).

Before using the leaching solution in an ammonium sulfate plant, Ishihara S.K. crystallized the ferrous sulfate as copperas and roasted it to produce sulfuric acid and ferric oxide. This last way could be preferred when ammonium sulfate cannot be used in local context.

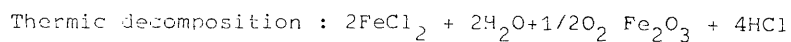
The production of ammonium sulfate is described in annex p A9/A10.

WOODALL DUCKHAM PROCESS

PICKLING LIQUORS REGENERATION
(OR TREATMENT OF METALLIC CHLORIDES)



Oxides



(Fuel)
(Air)

- 1 - SPRAY DYER
- 2 - CYCLONE
- 3 - PRE CONCENTRATION
- 4 - ABSORBER
- 5 - STACK

Feed : Ferrous chloride 20-23%
Metal chlorides 4%
Hydrochloric acid 2%
water : balance

Products : hydrochloric acid 18.5% (wt)
Ferric oxide + metal oxides

Typical unit 8 000h/y - production : hydrochloric acid : 31,000 t/y (100%)
Ferric oxide : 28,000 t/y

Feed rate : Pickling liquor : 17.2 m³/h
HCl produced : 19.4 m³/h
Process water : 20 m³/h

Consumption : Fuel 1,1 t/h
steam 2,5 t/h
Electricity : 730 Kw^h/h

Labor 2 men/shift

Investment 3.1 MUC

5-5 Iron oxide

Ferric oxide is the main by-product of the upgrading processes, but also a by product of many copperas or salt solutions treatments.

The question of its use has been already widely discussed.

Presently the ferric oxide produced in the main synthetic rutile plants in operation is just used as landfill.

The producers consider that it is mainly the small quantities available in each plant which limit its use since there is no special environmental pressure concerning this landfill operation.

In other countries such as Germany and Japan the ferric acid obtained as by product of roasting or neutralization is used in many ways.

For example, during 1974, Ishihara S.K. sold a ferrous ferric oxide compound which is extracted from its waste sulfuric acid neutralization process. This Iron oxide has been sold mainly for Iron manufacture.

Corresponding sales amounted to 473,000 US\$. Iron oxide by-product of Copperas roasting is also sold for pigment production.

It must be noted that when the ferric oxide is obtained from a compound which is separated by cristallization, the quality of the product can be easily improved by a selective cristallization and then a separate treatment.

To give some rough quantitative figures, let us consider a TiO_2 pigment obtained from an australian or an equivalent ore this operation requires 2t of ilmenite which contains 0,63 t of iron, and which could yield 0,9t of ferric oxide. This is an global figure.

Considering that Europe is using ilmenite, the corresponding amount of ferric oxide would be about 800,000 t/y (1976).

This ferric oxide is mainly located at the upgrading plant sites.

5-6 IRON

The slag process is a reduction and a smelting of ilmenite and it produces Iron directly.

Q.I.T. is the only company which operates a large scale plant based on this process (Canada). This firm sells two kinds of Iron :

"SORELMETAL D 1 (low carbon content)

"SORELMETAL F 1 (high carbon content)

The iron production of the sorel plant is 0.7 ton of iron per ton of slag. e.g. about 595,000 t/y

5-7 GAS

In many countries the regulations concerning the gaseous effluents are already well defined and are very stringent (e.g. Japan, germany).

Technically this problem is well known and many realizations made for reducing the amount of gaseous emission have already been completed ; sometimes, however, this type of treatment replaces a gaseous effluent problem by a liquid effluent problem.

The main gaseous effluents are listed below :

5-7-1 SO₂

In the sulfate process, the calcination step is an important source of SO₂. Sulfuric acid is so strongly adsorbed on titanium hydroxide that it can be only liberated by heating. The amount of H₂SO₄ adsorbed this way is around 7%/wt of TiO₂. Presently SO₂ is absorbed and water is dumped as weak acid.

5-7-2 CO

CO is unavoidably produced by the reduction reactions with C. (Slag process, chloride process).

Generally CO is locally used as auxiliary fuel.

5-7-3 HCl

The gaseous HCl can easily be absorbed and recycled or neutralized.

TABLE 5-2

EXAMPLES OF ENVIRONMENTAL MEASURES TAKEN IN VARIOUS COUNTRIES	
E E C	The European community is presently elaborating a directive
GERMANY BELGIUM	Sea disposals have to be authorized
FRANCE	It is forbidden to increase the amount of effluent rejected. Presently an extension (20 000 tpa) of the Thann et Mulhouse plant cannot be operated for this reason
NETHERLAND	The increase of the amount of effluent rejected is forbidden and disposal is subjected to an increasing tax
ITALY	Dumping in the sea has been temporary forbidden by local authorities. Waste acid are presently dumped after a complete neutralization. The main project of Montedison is based on chloride process.
UNITED KINGDOM	This country considers having favorable location allowing the dumping into the sea
SPAIN	The Tioxide plant Huelva (50.000 tpa) is the newest plant based on the sulfate process which dumps the waste acid. This tolerance may be considered as quite exceptional
FINLAND	The finish company Vuorikemia Oy is supposed to stop effluent disposal within 3 years
YUGOSLAVIA	No specific information are available but in Yugoslavia Cinkarna roasts its Copperas, and in Poland waste acid is concentrated and used in a fertilizer plant
POLAND	
U S A	The first edition of the EPA effluent guidelines and standards on TiO_2 production (March 1974) has been cancelled. A second edition based on the performance of the Am. Cyanamid plant as Best Available Tech, will be applied in Nov. 1977. Some limited and temporary derogations are possible. Each state can decide more stringent local regulations. All the new plants are based on the chloride process.
CANADA	Presently the main regulations concern the gaseous emissions but the definition and the application of the canadian objectives are very close of the EPA regulations. Each "Province" can decide local regulations (the two canadian TiO_2 producers are in the same Province).
JAPAN	Probably the most concerned country for the environmental questions. In 1970 the "Anti-pollution Diet" defined the environmental quality standards for water quality. An Environmental agency was created in 1974. There is no specific standard for the Titanium dioxide industry but the dumping in the sea is forbidden. All the plants have treatment facilities. A new plant is based on sulfate process with treatment but there is some projects based on the chloride process.
AUSTRALIA	This country is becoming very concerned by the environmental problem. Each state can set local regulations. Before building its plant Laporte had obtained guarantees from "Western Australia" state. In Tasmania Tioxide is very constrained. Laporte is experimenting a process in order to valorize waste acid in Manganese dioxide industry.
INDIA	There is no special environmental organization yet, but with the industrial development this country becomes more concerned. The existing plant based on sulfat process is examining the possibility of production of ammonium sulfat. Two projects of TiO_2 production are based on the chloride process.
BRAZIL	The main project of TiO_2 production (60 000 t. p. a.) is based on the chloride process (N J Z + Montedison)

SECTION 6

DESCRIPTION OF THE WORLD TiO₂ INDUSTRY

(End 1976)

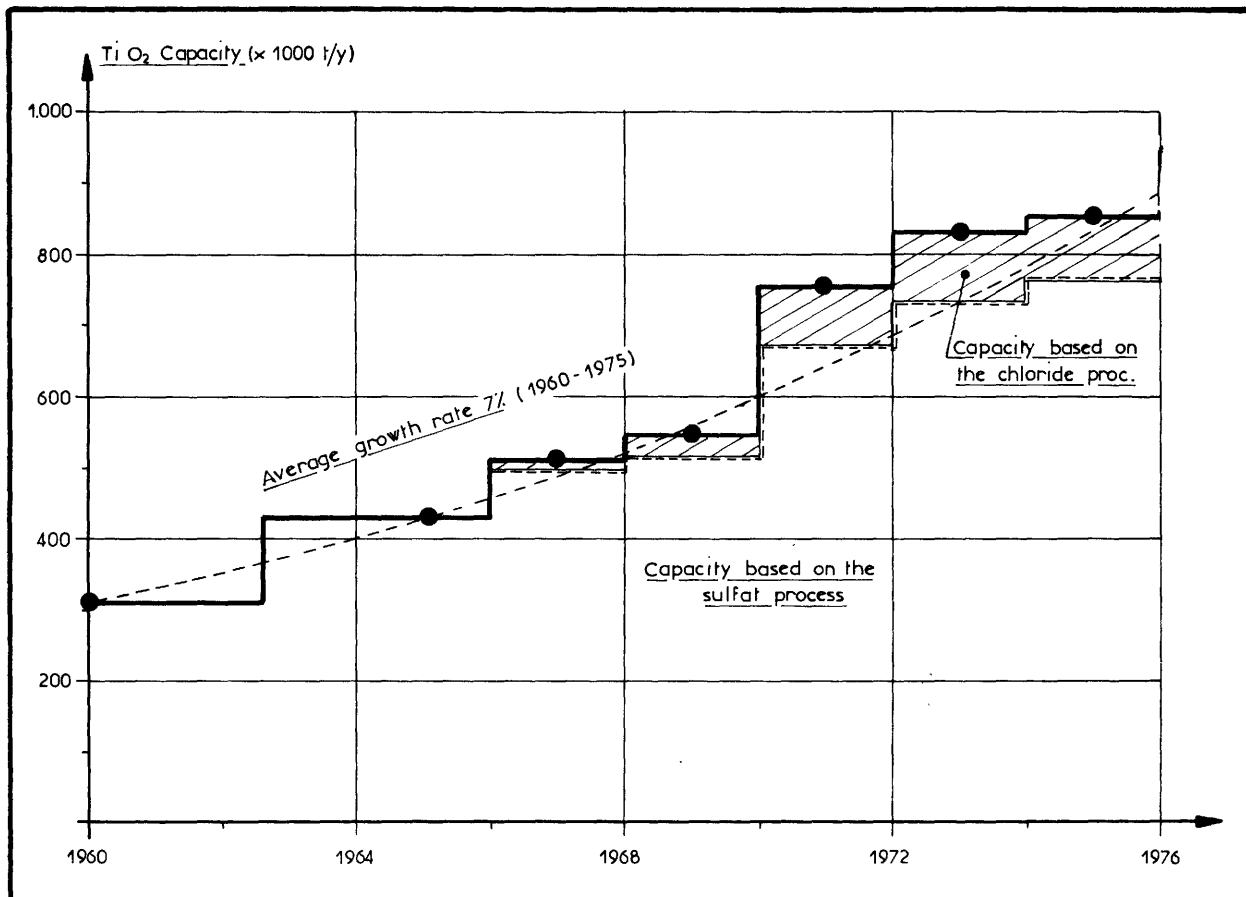
SECTION 6DESCRIPTION OF THE WORLD TiO₂ INDUSTRY

(End 1976)

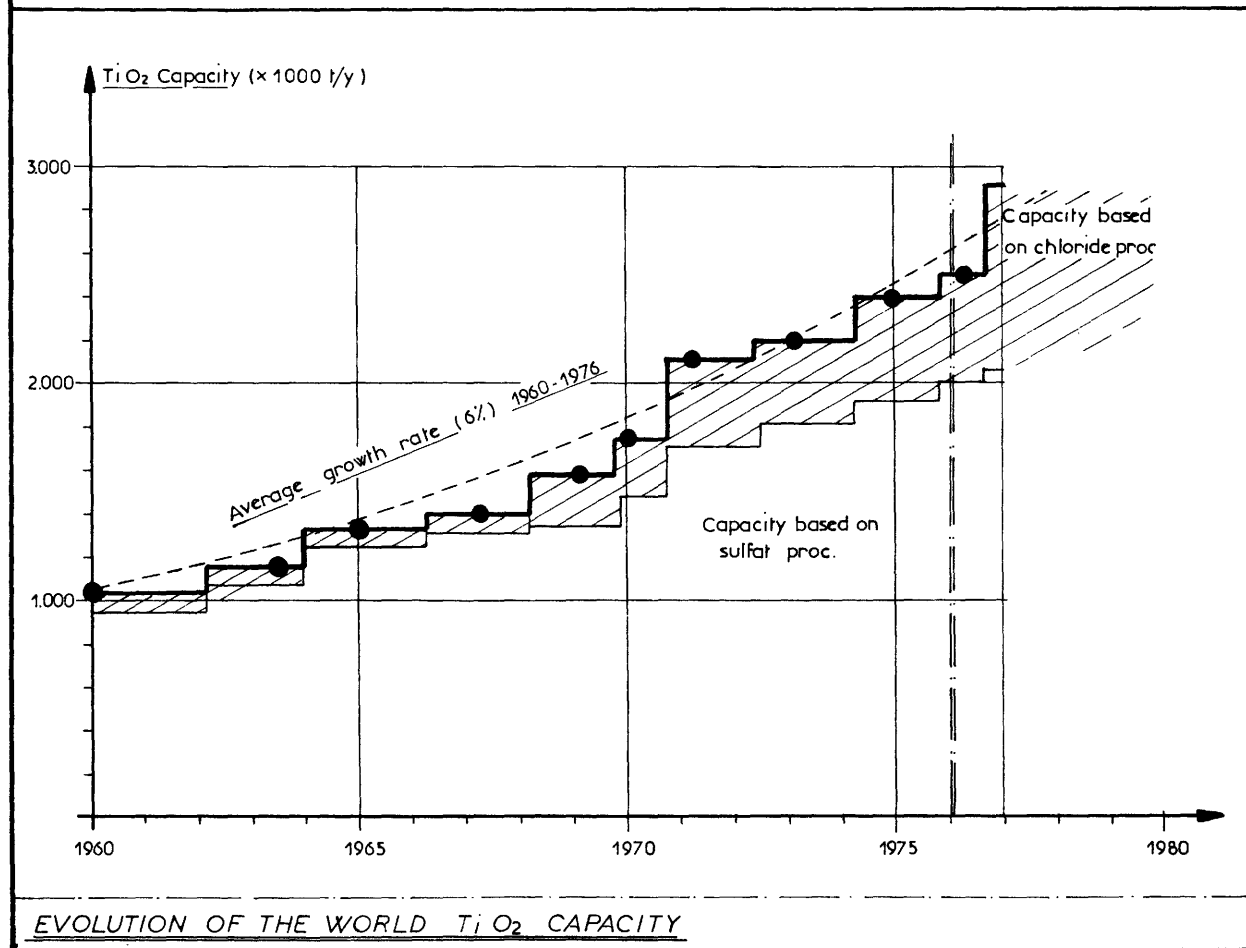
- 6-1 Summary of TiO₂ industry capacities between 1966-1976
- 6-2 Summary of the capacities in the world (End 1976)
- 6-3 Main features of the TiO₂ plants in the world

6-1 Summary of TiO₂ industry capacities between 1960-1976

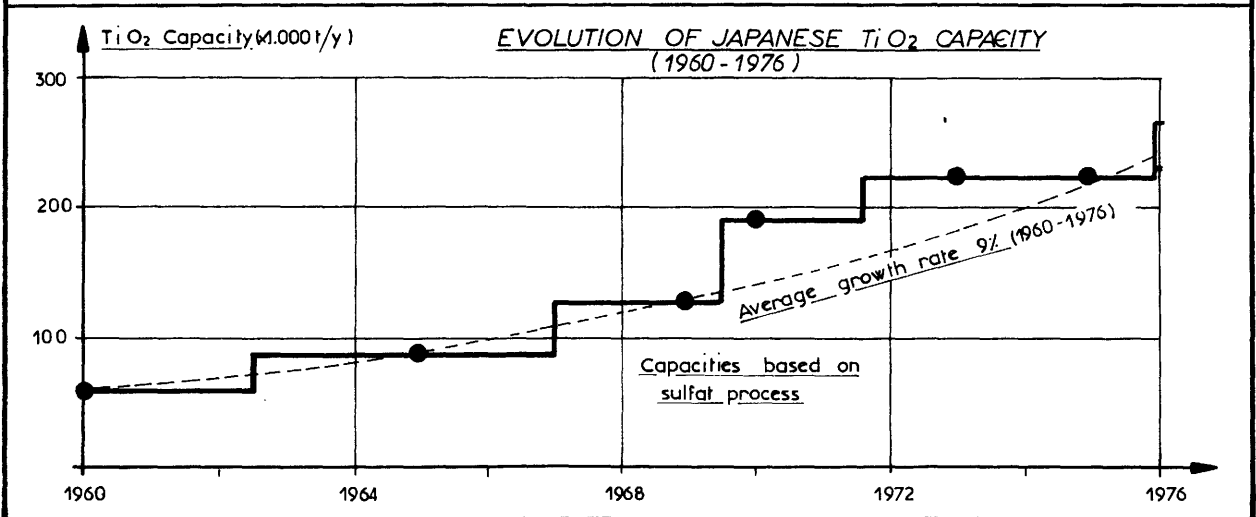
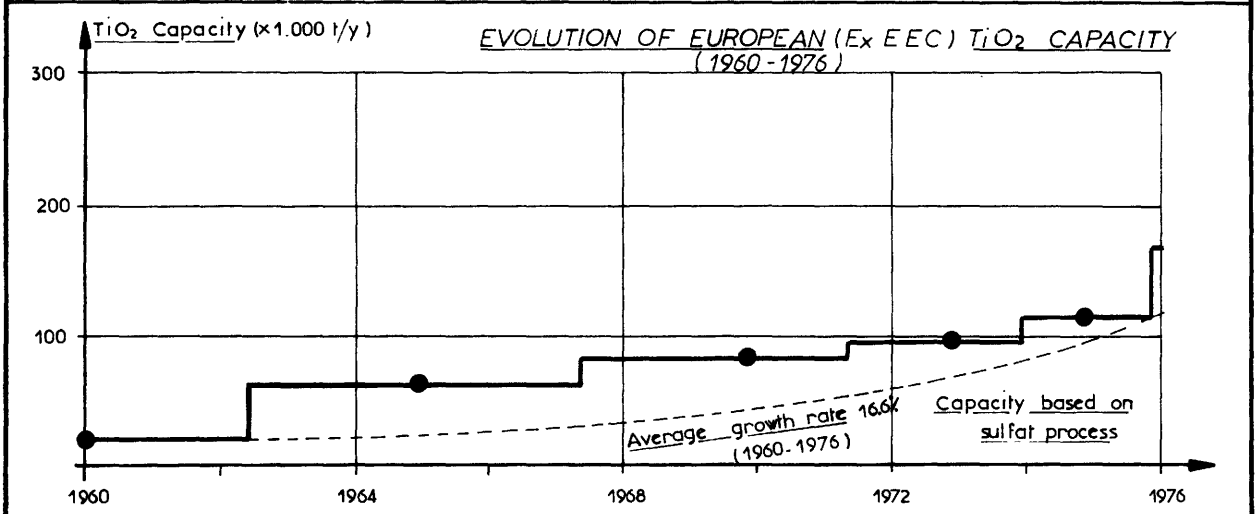
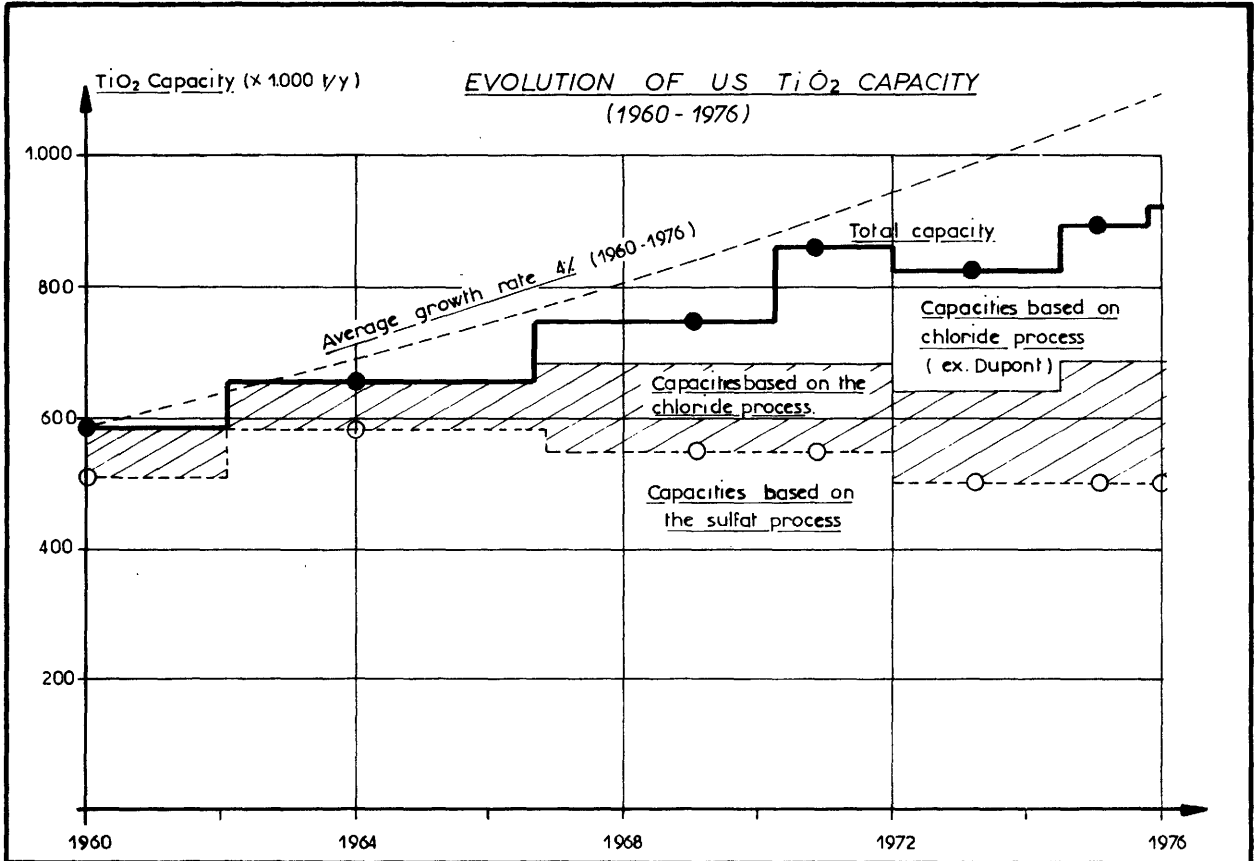
- Evolution of the EEC TiO₂ Capacity
- Evolution of the world TiO₂ Capacity
- Evolution of the US TiO₂ Capacity
- Evolution of European (Ex EEC) TiO₂ Capacity
- Evolution of Japanese TiO₂ Capacity



EVOLUTION OF THE EEC TiO₂ CAPACITY (Germany, Belgium, France, Netherland, Italy, U.K.)

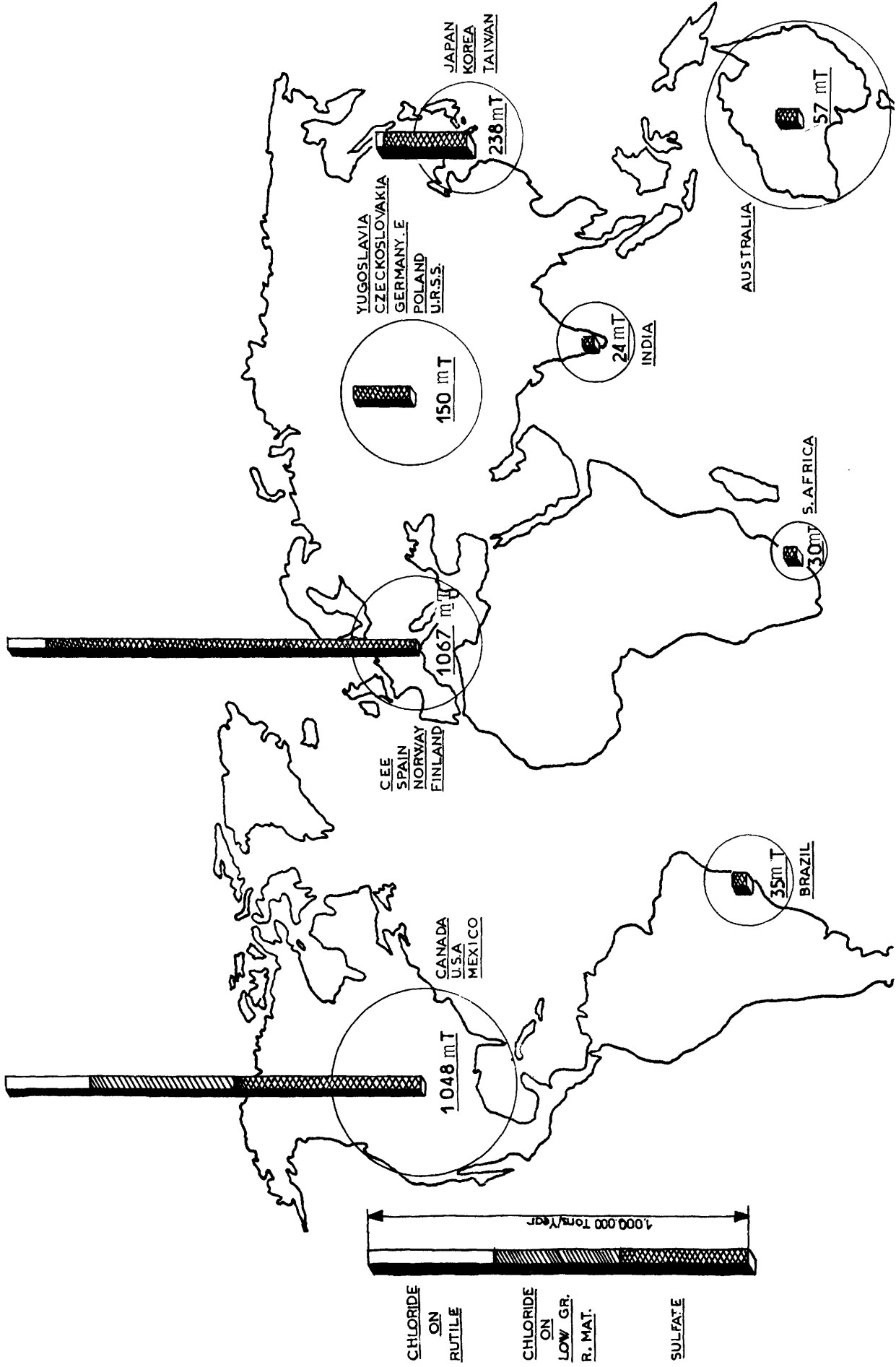


EVOLUTION OF THE WORLD TiO₂ CAPACITY



6-2 SUMMARY OF THE CAPACITIES IN THE WORLD (END 1976)

Country	Total capacity	Sulfate	Chloride on Rutile	Chloride on low gr. R. Mat.
Europe E.E.C.	895.000	791.000	104.000	--
Spain Norway Finland	172.000	172.000	--	--
U.S.A.	960.000	394.000	188.000	379.000
Canada	58.000	58.000	--	--
Mexico	30.000	30.000	--	--
Brazil	35.000	--	35.000	--
Japan	228.000	208.000	20.000	--
Korea, Taiwan	10.000	10.000	--	--
S. Africa	30.000	30.000	--	--
India	24.000	24.000	--	--
Australia	57.000	57.000	--	--
SUB TOTAL	2.500.000	1.774.000	347.000	379.000
Yugoslavia Czechoslovakia Germany E. Poland USSR	(150.000?)	150.000 ?	--	--
TOTAL	2.650.000	1.924.000	347.000	379.000



TiO₂ CAPACITIES IN THE WORLD (End 1976)

TiO₂ PLANT LIST

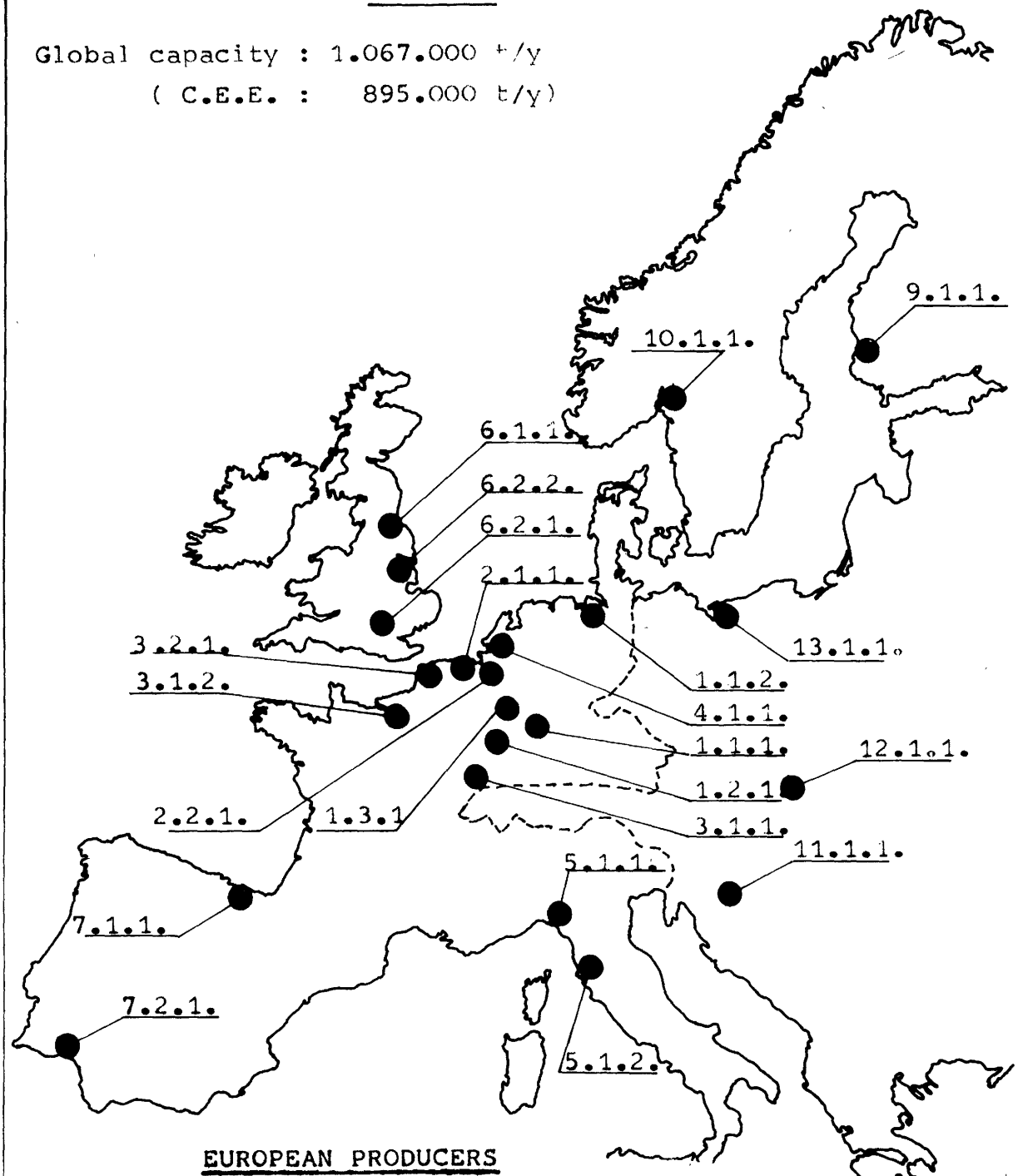
<u>GERMANY</u>	Ref 1. 1. 1. : Kronos Titan 1. 1. 2 : Kronos Titan 1. 2. 1 : Bayer S. A. 1. 3. 1 : Pigment chemie	<u>POLAND</u>	Ref 13. 1. 1: State owned plant
<u>BELGIUM</u>	Ref 2. 1. 1 : Kronos Titan 2. 2. 1 : Bayer S. A.	<u>USA</u>	Ref 15. 1. 1: American Cyanamid 15. 2. 1: Du Pont 15. 2. 2: Du Pont 15. 4. 2: Kerr Mc gee 15. 5. 1: National Lead 15. 5. 2: National Lead 15. 6. 1: SCM glidden Durkee 15. 6. 2: SCM glidden Durkee
<u>FRANCE</u>	Ref 3. 1. 1 : Thann et Mulhouse 3. 1. 2 : Thann et Mulhouse 3. 2. 1 : Tioxide	<u>CANADA</u>	Ref 16. 1. 1 : Canadian Titanium 16. 2. 1 : Tioxide of Canada
<u>NETHERLAND</u>	Ref 4. 1. 1. : Tiofine	<u>MEXICO</u>	Ref 17. 1. 1: Pigmentos y Productos Quimicos
<u>ITALY</u>	Ref 5. 1. 1 : Montedison 5. 1. 2 : Montedison	<u>BRAZIL</u>	Ref 18. 2. 1: "Tibras" Titanio do Brazil
<u>UNITED KINGDOM</u>	Ref 6. 1. 1 : Tioxide 6. 1. 2 : Tioxide 6. 1. 3 : Tioxide 6. 2. 1 : Laporte Titanium 6. 2. 2 : Laporte Titanium	<u>JAPAN</u>	Ref 20. 1. 1: Furukawa Mining Co 20. 2. 1: Ishihara Sangyo Kaisha 20. 3. 1: Sakai Chemical Industry 20. 4. 1: Teikoku Kako Co 20. 5. 1: Titan Kogyo KK 20. 6. 1: Fuji Titanium 20. 7. 1: Tohoku Kagaku
<u>SPAIN</u>	Ref 7. 1. 1 : Dow Unquinesa 7. 2. 1 : Titania S. A.	<u>KOREA</u>	Ref 22. 1. 1 Hankok Titanium
<u>FINLAND</u>	Ref 9. 1. 1 : Vuorikemia Oy	<u>INDIA</u>	Ref 23. 1. 1 Travancore Titanium Products
<u>NORWAY</u>	Ref 10. 1. 1: Titan AS	<u>SOUTH AFRICA</u>	Ref 26. 1. 1 South African Titan products
<u>YUGOSLAVIA</u>	Ref 18. 1. 1: Cinkarna	<u>TAIWAN</u>	Ref 27. 1. 1 China Metal Chemical 27. 2. 1 Central Asia
<u>CZECHOSLOVAKIA</u>	Ref 12. 1. 1: Prerovske Chemische Zadovy 12. 2. 1: Spolek	<u>AUSTRALIA</u>	Ref 25. 1. 1 Australian Titan 25. 2. 1 Laporte Titanium

Main published project

SOLVAY/LAPORTE	Chl. - 50,000 t/y
MONTEDISON	Chl. - 40,000 (Crotone)
SIR	Chl. - 20,000 t/y (Porto Torres)
LAPORTE	Chl. - 44,000 t/y (Stallinborough)
KRONOS TITAN	Chl. - 36,000 t/y (Leverkusen)
POLIMEX	36,000 t/y (Poland)
DUPONT	150,000 t/y (USA)
NL INDUSTRIE	100,000 t/y (USA)
SAKAI - KERALA MINERALS	

EUROPE

Global capacity : 1.067.000 t/y
 (C.E.E. : 895.000 t/y)

EUROPEAN PRODUCERS

KROMOS TITAN(N.LEAD) (1.1...,2.1...,10.1..)	- 215.000 t/y
TIOXIDE(ICI,LEAD IND.) (3.2..., 6.1..)	- 207.000 t/y
BAYER (1.2..., 2.2..)	- 115.000 t/y
LAPORTE (HOLDING) (6.2..)	- 105.000 t/y
THANN ET MULHOUSE (68,5% R.POULENC) (3.1..)	- 100.000 t/y
MONTEDISON (5.1..)	- 93.000 t/y
VUORIKEMIA (State-owned) (9.1..)	- 80.000 t/y
PIGMENT CHEMIE (70% SACTLEBEN) (1.3..)	- 50.000 t/y
TITANIO (45% TIOXIDE) (7.2..)	- 40.000 t/y
TIOFINE (50% AMERICAN CYANAMID) (4.1..)	- 35.000 t/y
DOW UNQUINESA (DOW CHEMICAL) (7.1..)	- 27.000 t/y

EUROPEGERMANYRef. : 1.1.1.

Co. : KRONOS TITAN

1. Pr. : Sulfate

R. Mat. : Ilmenite from Norway
 Loc. : Leverkusen (alongside the Rhein about 300 km.
 from Rotterdam)
 Fil. : National Lead
 Cap. : 70.000 t/y
 Treat. : Wastes are carried from Leverkusen to Rotterdam
 and then dumped in the sea.

2. Pr. : Chloride
Cap.: 14.000 t/y

Remarks : Kronos titan has developed a new chloride
 process which can use low grade raw material.

Ref. : 1.1.2.

Co. : KRONOS TITAN

Pr. : Sulfate

R. Mat. : Ilmenite from Norway
 Loc. : Nordenham on the estuary of the Weser river
 Fil. : National Lead
 Cap. : 66.000 t/y
 Treat. : Wastes are dumped in the sea with a boat.

Ref. : 1.2.1.

Co. : BAYER S.A.

1. Pr. : Sulfate

R. Mat. : Canadian Slag
 Loc. : Uerdingen
 Cap. : 70.000 t/y
 Treat. : Waste acid is concentrated.
 Salts are roasted.

2. Pr. : Chloride
Cap.:20.000 t/y

Ref. : 1.3.1.

Co. : PIGMENT CHEMIE

Pr. Sulfate (Du Pont)
R. Mat. : Canadian Slag
Loc. : Homberg (alongside the Rhein about 300 km.
from Rotterdam)
Cap. : 50.000 t/y
Treat. : Strong acid is carried to Rotterdam and then
dumped in the sea.
Weak acid is dumped in the Rhein

BELGIUMRef. : 2.1.1.

Co. : KRONOS TITAN

Pr. : Sulfate
R. Mat. : Canadian Slag
Loc. : Langerbrugge (on seaside)
Fil. : 82% National Lead
Cap. : 40.000 t/y
Treat. : Waste are dumped in the sea.

Ref. : 2.2.1.

Co. : BAYER S.A.

Pr. : Sulfate
R. Mat. : Canadian Slag
Loc. : Anvers
Cap. : 25.000 t/y
Treat. : Wastes are dumped in the sea

FRANCERef. : 3.1.1.

Co. : THANN ET MULHOUSE

Pr. : Sulfate
R. Mat. : Mainly Ilmenite from Australia
Loc. : Thann (inland)
Cap. : 20.000 t/y
Treat. : Complete neutralization. The products
of neutralization are stockpiled outside.
A part of the copperas is sold for water
treatment.

Ref. : 3.1.2.

Co. : THANN ET MULHOUSE

Pr. : Sulfate
R. Mat. : Mainly Ilmenite from Australia
Loc. : Le Havre (on the Seine estuary)
Cap. : 80.000 t/y, (only 60.000 t/y in operation)
Treat. : Wastes are dumped in the sea by pipe
Remark : A 20.000 t/y extension cannot be used because of
local environmental regulations.

Ref. : 3.2.1.

Co. : TIOXIDE

Pr. Sulfate (B.T.P. process)
R. Mat. : Canadian Slag
Loc. : Calais (on seaside)
Fil. : Tioxide ex British Titan products
Cap. : 60.000 t/y
Treat. : Wastes are directly dumped in the sea by pipe.

NETHERLAND

Ref. : 4.1.1.

Co. : TIOFINE

Pr. : Sulfate (Glidden process)
R. Mat. : Canadian Slag
Loc. : Rozenburg (alongside the river Maas near the
seaside)
Fil. : 50% American Cyanamid: 27,5% Billiton,
22,5% AKZO
Cap. : 35.000 t/y
Treat. : Wastes are dumped in the Rhein Delta (This plant
is subjected to taxation and limitations).

ITALY

Ref. : 5.1.1.

Co. : MONTEDISON

Pr. : Sulfate
R. Mat. : Canadian Slag and Ilmenite from Norway
Loc. : Spinetta marengo (alongside a river)
Cap. : 43.000 t/y
Treat. : Copperas are deshydrated by Lurgi process and
roasted by Dorr Oliver process.
A part of the strong acid is concentrated and the
other part is neutralized.

Remarks : This plant shall be closed before 1980.

Ref. : 5.1.2.

Co. : MONTEDISON

Pr. : Sulfate

R. Mat. : Ilmenite from Norway and Canadian Slag

Loc. Scarlino (on seaside)

cap. 54.000 t/y

Treat. Copperas are stockpiled.

Waste acid is neutralized. Products of neutralization are either dumped in the sea or stockpiled with copperas.

Remarks : The limitation on the effluents limits the effective capacity to 35.000 t/y instead of 54.000 t/y

UNITED KINGDOM

Ref. : 6.1.1.

Co. TIOXIDE ex British Titan Products

Pr. : Chloride

R. Mat. : Rutile

Loc. : Greatham

Fil. : 43,6% I.C.I., 43,6% Lead industry group,
12,8% Greef chemicals

Cap. : 30.000 t/y

Remarks : After many years of experimental runs Tioxide has decided to make important modifications of this plant.

Ref. : 6.1.2.

Co. : TIOXIDE ex British Titan Products

Pr. : Sulfate

R. Mat. : Canadian Slag or Ilmenite from Australia

Loc. : Billingham (on the Tees estuary)

Cap. : 27.000 t/y

Treat. : Waste acid is dumped in the sea by pipe

Ref. : 6.1.3.

Co. TIOXIDE ex British Titan Products

Pr. : Sulfate

R. Mat. : Ilmenite from Australia

Loc. : Grimsby (on the Humber estuary)

Cap. : 90.000 t/y

Treat. : A part of the copperas is sold, the other part is dumped by pipe in the sea with the waste acid.

Ref. : 6.2.1.

Co. : LAPORTE TITANIUM

Pr. Sulfate

R. Mat. : Canadian Slag or Ilmenite from Norway

Loc. : Lincs (on the Humber estuary)

Cap. : 65.000 t/y

Treat. : Copperas and waste acid are dumped in the sea by pipe.

Ref. : 6.2.2.

Co. : LAPORTE TITANIUM

Pr. Chloride (Collaboration with Kerr McGee)

R. Mat. : Natural Rutile and synthetic Rutile from "Taiwan alkali".

Loc. : Stallingborough

Cap. : 40.000 t/y

Treat. : no effluent.

SPAINRef. : 7.1.1.

Co. DOW UNQUINESA

Pr. : Sulfate

R. Mat. : Local ilmenite and Ilmenite from Norway

Loc. : Axpe- Bilbao

Fil. : Dow Chemical

Cap. : 27.000 t/y

Ref. : 7.2.1.

Co.: TITANIO S.A.

Pr. : Sulfate (B.T.P.)

R. Mat. : Local Ilmenite and Ilmenite from Norway

Loc. : Huelva (on seaside)

Fil. : 45% Tioxide ex B.T.P.

55% Union Explosives Rio Tinto S.A.

Cap. : 40.000 t/y

Treat. : A part of copperas is sold for water treatment and agricultural usage, the remainder is roasted. The waste acid is dumped in the sea by ships.

FINLANDRef. : 9.1.1.

Co. : VUORIKEMIA O.Y.

Pr. : Sulfate (B.T.P. process)
 R. Mat. : Mainly local ilmenite and a small amount of
 ilmenite from Norway
 Loc. : Pori (on seaside)
 Cap. : 80.000 t/y
 Treat. : Copperas and waste acid are dumped in the sea
 by pipe.
 Remarks : Effluent disposal must be stopped within 3 years.

NORWAYRef. : 10.1.1.

Co. : TITAN A.S.

Pr. Sulfate (National Lead)
 R. Mat. : local Ilmenite
 Loc. : Fredrikstad (on seaside)
 Cap. : 25.000 t/y
 Fil. : National Lead

YUGOSLAVIARef. : 18.1.1.

Co. : CINKARNA

Pr. Sulfate (Thann et Mulhouse)
 Cap. : 20.000 t/y
 Loc. : Celje
 Remarks : A total capacity of 50.000 t/y is planned for
 1979
 Copperas are dried (Lurgi process) and roasted

CZECHOSLOVAKIARef. : 12.1.1.

Co. : PREROVSKE CHEMICKE ZADOVY

Pr. : Sulfate
 Cap. : 30.000 t/y
 Loc. : Prerov

Ref. : 12.2.1.

Co. : SPOLEK

Pr. : Sulfate
 Cap. : 12.000 t/y
 R. Mat. : Finnish Ilmenite
 Loc. : Ostrava

POLANDRef. : 13.1.1.

Co. : STATE OWNED

A plant of 40.000 t/y designed by Kronos and constructed by Krupp Chemieanlagenbau is supposed to be at the construction phase. This plant will use Norwegian ilmenite.

Ref. : 13.2.1

Co. : STATE OWNED

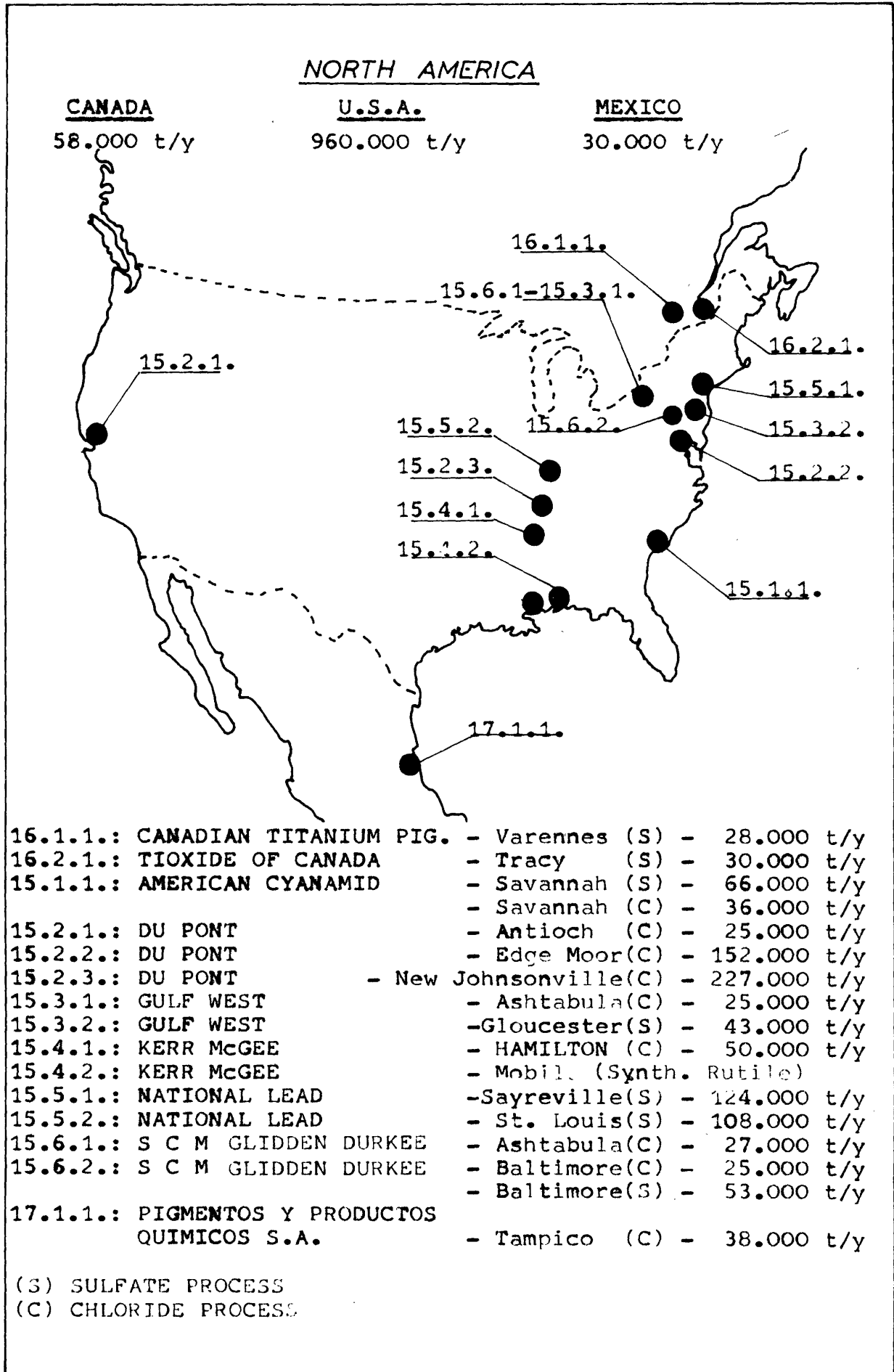
Capacity is supposed to be 30,000t/y based on sulfat process loc. Police.

R.Mat : Russian Ilmenite

Treat : Strong acid is supposed to be sold to a fertilizer plant

U.R.S.S

Ref. : 14.1.1



U S ARef. : 15.1.1.

Co. : AMERICAN CYANAMID

1. Pr. : Sulfate
R. Mat. : Imported ilmenite and titanium slag
Loc. : Savannah (Georgia)
Cap. : 66.000 t/y
Treat. : Complete neutralization and settling of :
 - strong acid
 - weak acid
 - cooling waterNeutralized water is dumped in the river.
Neutralization products are stockpiled.
2. Pr. : Chloride (Kerr McGee)
R. Mat. : Imported Rutile (Australia)
Loc. : Savannah (Georgia)
Cap. : 36.000 t/y
Treat. : no effluent

Ref. : 15.2.1.

Co. : DU PONT

Pr. : Chloride
R. Mat. : Imported Rutile (Australia)
Loc. : Antioch (California)
Cap. : 25.000 t/y
Treat.: no effluent

Ref. : 15.2.2.

Co. : DU PONT

Pr. : Chloride
R. Mat. : Captive mixture of Ilmenite, leucoxene, **Rutile**
Loc. : Edge Moor (Delaware)
Cap. : 152.000 t/y
Treat. : A part of the waste is converted to ferric chloride
and sold. The other part is dumped in the sea.

Ref. : 15.2.3.

Co. : DU PONT

Pr. Chloride

R. Mat. : Captive mixture of Ilmenite, leucoxene, Rutile

Loc. : New Johnsonville (Tennessee)

Cap. : 227.000 t/y

Treat. : Presently the waste are dumped by deep well injection. Du Pont is operating a pilot plant to test the ferric chloride oxidation in ferric oxide and chlorine.

Ref. : 15.3.1.

Co. : GULF WEST

Pr. : Chloride (Thann et Mulhouse process)

R. Mat. : Imported Rutile (Australia)

Loc. : Ashtabula

Cap. : 25.000 t/y

Treat. : no effluents

Remarks : This plant has been bought to Cabot.

Ref. : 15.3.2.

Co. : GULF WEST

Pr. Sulfate

R. Mat. : Slag

Loc. : Gloucester

Cap. : 43.000 t/y

Treat. : During many years this company has operated a pilot to test a acid regeneration process, but experimental results were not good and presently the programm is completely stopped. Waste acid would be dumped in the Delaware river maybe after a first neutralization.

Ref. : 15.4.1.

Co. : KERR MCGEE

Pr. : Chloride (Kerr McGee process)

R. Mat. : Imported Rutile and synthetic Rutile

Loc. : Hamilton Mississippi

Cap. : 50.000 t/y

Treat. : no effluent

Ref. : 15.4.2.

Co. : KERR McGEE

Pr. : Synthetic Rutile (Benilite)
R. Mat. : Imported Ilmenite, then captive ilmenite
Loc. : Mobile
Cap. : 50.000 t/y
Treat. : Hydrochloric acid is regenerated, ferric oxide will
be stockpiled.

Ref. : 15.5.1.

Co. : NATIONAL LEAD

Pr. : Sulfate
R. Mat. : Captive Ilmenite
Loc. : Sayreville
Cap. : 124.000 t/y
Treat. : Wastes are dumped in the sea (with monitoring)
Remarks : Presently (end 1976) this plant has been shutdown
because a long strike. Before shutdown the production
was only about fifty percent of the capacity and
it seems that this plant could be definitely closed
in the next future.

Ref. : 15.5.2.

Co. : NATIONAL LEAD

Pr. : Sulfate
R. Mat. : Canadian Slag
Loc. : St. Louis
Cap. : 108.000 t/y
Treat. : Wastes acid is dumped in the Mississippi river

Ref. : 15.6.1.

Co. : S C M GLIDDEN DURKEE

Pr. : Chloride (Du Pont Process)
R. Mat. : Imported Rutile
Loc. : Ashtabula (Ohio)
Cap. : 27.000 t/y
Treat. : no effluent
Remarks : This plant has been bought to Sherwin William

Ref. : 15.6.2.

Co. : S C M GLIDDEN DURKEE

Loc. : Baltimore (Maryland)

1. Pr. : Chloride (Kerr McGee process)

R. Mat. : Imported Rutile

Cap. : 25.000 t/y

Treat. : no effluent

2. Pr. : Sulfate

R. Mat. : Captive ilmenite and canadian Slag

Cap. : 53.000 t/y

Treat. : A part of the strong acid is directly sold for use in phosphoric acid production.

A part of the strong acid is regenerated, the other part is neutralized and the product of neutralization are stockpiled.

In the future the weak acid will be neutralized (end 1977)

C A N A D A

Ref. : 16.1.1.

Co. : CANADIAN TITANIUM PIG.

Pr. : Sulfate

R. Mat. : Canadian Slag

Loc. : Varennes (alongside the St. Laurent)

Fil. : 100% National Lead

Cap. : 28.000 t/y

Treat. : Effluents are directly dumped in the St. Laurent by pipe and without neutralization

Remarks : The Chloride plant was shut down in 1972 after many operating troubles

Ref. : 16.2.1.

Co. : TIOXIDE OF CANADA

Pr. : Sulfate

R. Mat. : Canadian Slag

Loc. : Tracy (alongside the St. Laurent)

Fil. : 100% B.T.P.

Cap. : 30.000 t/y

Treat. : Effluents are directly dumped in the St. Laurent by pipe and without neutralization

M E X I C O

Ref. : 17.1.1.

Co. : PIGMENTOS Y PRODUCTOS QUIMICOS S.A.

Pr. : Chloride

R. Mat. :

Loc. : Tampico

Fil. : 49% Du Pont, 51% Banco de Comercio

Cap. : 30.000 t/y

Remarks : This plant is believed to have been revamped and converted to the chloride process (mid 76)

B R A Z I L

Ref. : 18.2.1.

Co. : 'TIBRAS' TITANIC DO BRAZIL

Pr. : Sulfate (Laporte process)

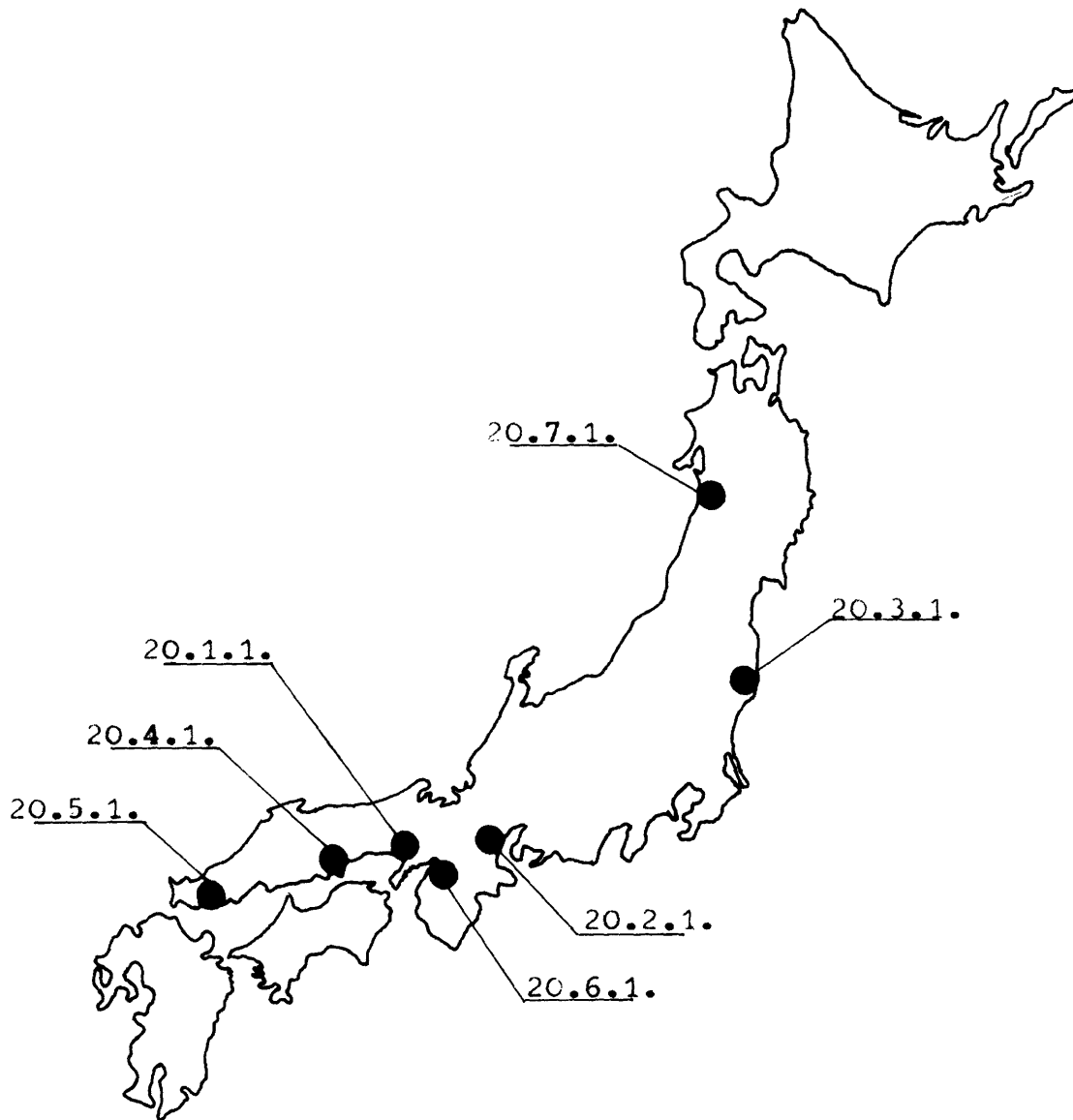
R. Mat. : Ilmenite from the state of Bahia

Loc. : Camacari

Cap. : 35.000 t/y

JAPAN

Global capacity : 228.000 t/y



20.1.1.	: FURUKAWA MINING Co.	- Osaka	- 24.000 t/y
20.2.1.	: ISHIHARA SANGYO KAISHA	- Yokkaichi	- 90.000 t/y + 20.000 t/v
20.3.1.	: SAKAI CHEMICAL IND.	- Onahama	- 30.000 t/y
20.4.1.	: TEIKOKU KAKO Co.	- Saidaji	- 27.000 t/y
20.5.1.	: TITAN KOGYO KK	- Ube	- 13.000 t/y
20.6.1.	: FUJI TITANIUM IND.	- Kobe	- 12.000 t/y
20.7.1.	: TOHOKU KAGAKU	- Akita	- 12.000 t/y

J A P A N

Ref.: 20.1.1

Co.: FURUKAWA MINING Co

Pr.: Sulfate

R.Mat.: Ilmenite from Malaysia and India

Loc. : on seaside between Osaka and Kobe

Fil. : Furukawa

Cap. : 24.000 t/year in operation

Treat.: Neutralization - by-products are stockpiled.

Ref.: 20.2.1

Co.: ISHIHARA SANGYO KAISHA

1. Pr.: Sulfate (Pr. Glidden)

first production 1954 (6.000 t/y)

R.Mat.: -Canadian Slag

-Ilmenite from Ceylan and India (M.K. grade)

Loc. : on seaside near Yokkaichi

Fil. : Ishihara

Cap. : 90.000 t/y

treat.

Copperas

A part is used by Yokkaichi Chemical Co to produce sodium sulfate with Ishihara technology.

A part is sold for water treatment as coagulating agent and for red iron oxide.

Waste acid

A part is used in the synthetic rutile plant.

A part is concentrated up to 62%. The separated salts are dissolved in the stream of sulfuric acid from the synthetic rutile plant. The stream is used in the fertilizer plant which produces :

- Ammonium sulfate
- Magnesium ammonium sulfate
- Hydrated iron oxide
- Ammonium metavanadate

2. Pr. : Chloride (Kerr McGee)

first production : beg. 1975 (12.000 t/y)
(investment : 24,6 millions US-dollars)

R. Mat. : own synthetic rutile

Cap. : 20.000 t/y

3. Pr. : Synthetic Rutile (Ishihara)

first production mid 1971 (25.000 t/y)

R. Mat. : Ilmenite from India (Q grade)

Cap. : 40.000 t/y

Waste acid is used in the fertilizer plant.

Trade name : Rupaque.

Ref : 20.3.1

Co. : SAKAI CHEMICAL INDUSTRY

Pr. : Sulfate

This new plant has been built in replacement of the old plant located near Osaka where the pollution control were too strict.

A part of the equipment has been transferred.

R. Mat. : Ilmenite from Malaysia and from Australia

Loc. : on seaside Iwaki City near Onahama

Fil. : Mitsubishi Metal Mining

Remarks : In this location a cheap sulfuric acid is available

Cap. : 30.000 t/y

Treat. : Copperas are roasted with production of sulfuric acid and ammonium sulfate.

Ammonium sulfate is sold.

Ferric oxide by-producted is used as pigment.

Strong acid is neutralized.

Trade name : Titone

Sakai plans to built a plant using the chloride process (Kerr Mc Gee) and the synthetic rutile process (benilite). The slowdown of this industry during the last years has postponed this project.

Ref.: 20.4.1

Co. : TEIKOKU KAKO Co.

Pr. : Sulfate (old plant)

R.Mat. : Ilmenite from Malaysia and from Australia

Loc. : on seaside Saidaji near Okayama

This plant is located near a very large
sulfuric acid plant

Fil. : Mitsubishi Chemical

Cap. : 27.000 t/y

Treat. : - Copperas are sold to DOWA Mining.
- Strong acid is neutralized with caustic
soda to produce sodium sulfate which is
sold as detergent.

Trade name : Teika

Teikoku is believed to be talking to Du Pont
to obtain a license for the chloride process
based on rutile.

Ref. : 20.5.1

Co. : TITAN KOGYO KK

Pr. : Sulfate (old plant -originally kronos process)

R.Mat. : Ilmenite from Malaysia and from India
(M.K. grade)

Loc. : on seaside near Ube

Fil. : Titan Kogyo

Cap. : 13.000 t/y

Treat : Copperas are roasted. Ferric oxide is used
as pigment and to produce salt ferrite
(tape record).

Waste acid is sold to UBE KOHSAN which produces
ammonium sulfate.

Trade name : Sunitox.

Ref. : 20.6.1

Co. : FUJI TITANIUM IND.

Pr. : Sulfate (Glidden Durkee)

R.Mat. : Ilmenite from Malaysia

Loc. : Kobe and Hiratsuka (finition) Plant in land

Fil. : 50% Ishihara

50% Asahi Chemical (synthetic fiber)

Cap. : 12.000 t/y

Treat. : Copperas - just dry and sold to produce iron oxide.

Waste acid - concentrated and recirculated
(steam evaporation)

- Salts are neutralized

- a part of the waste acid is
neutralized to produce gypsum.

This plant is located in an area with very strict environmental control. The technology used to concentrate waste acid has been developed in the university of Kobe.

Trade name : Fujititan.

Ref. : 20.7.1

Co. : TOHOKU KAGAKU

Pr. : Sulfate (new plant with Sakai Technology)

R.Mat. : Ilmenite from Malaysia

Loc. : Akita

Fil. : Mitsubishi Metal Mining (Mitsubishi, Sakai, Takaku, Hiryo)

Cap. : 12.000 t/y (prod. 6.000 t/y new producer in this field)

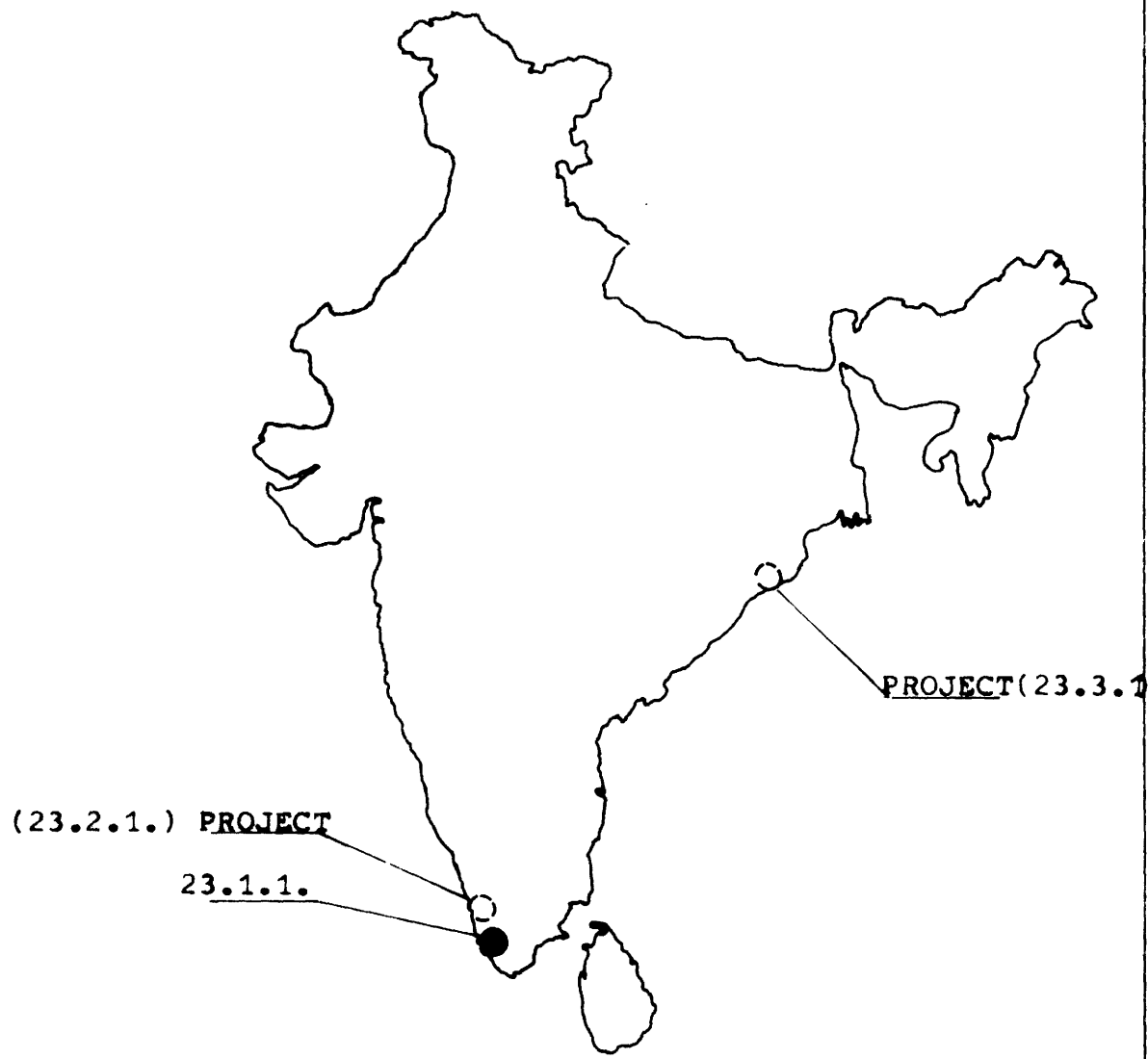
Treat. : Copperas are roasted

Strong acid is concentrated and recycled.

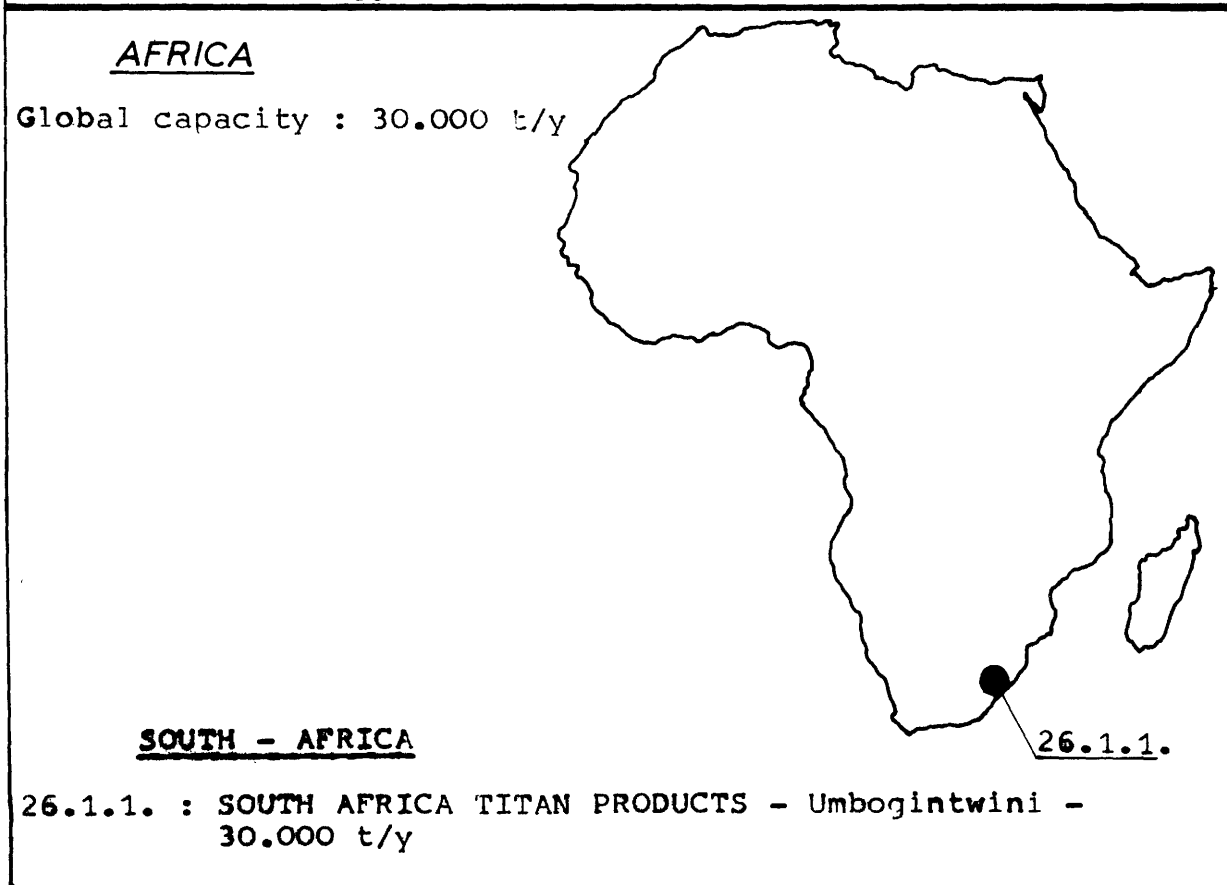
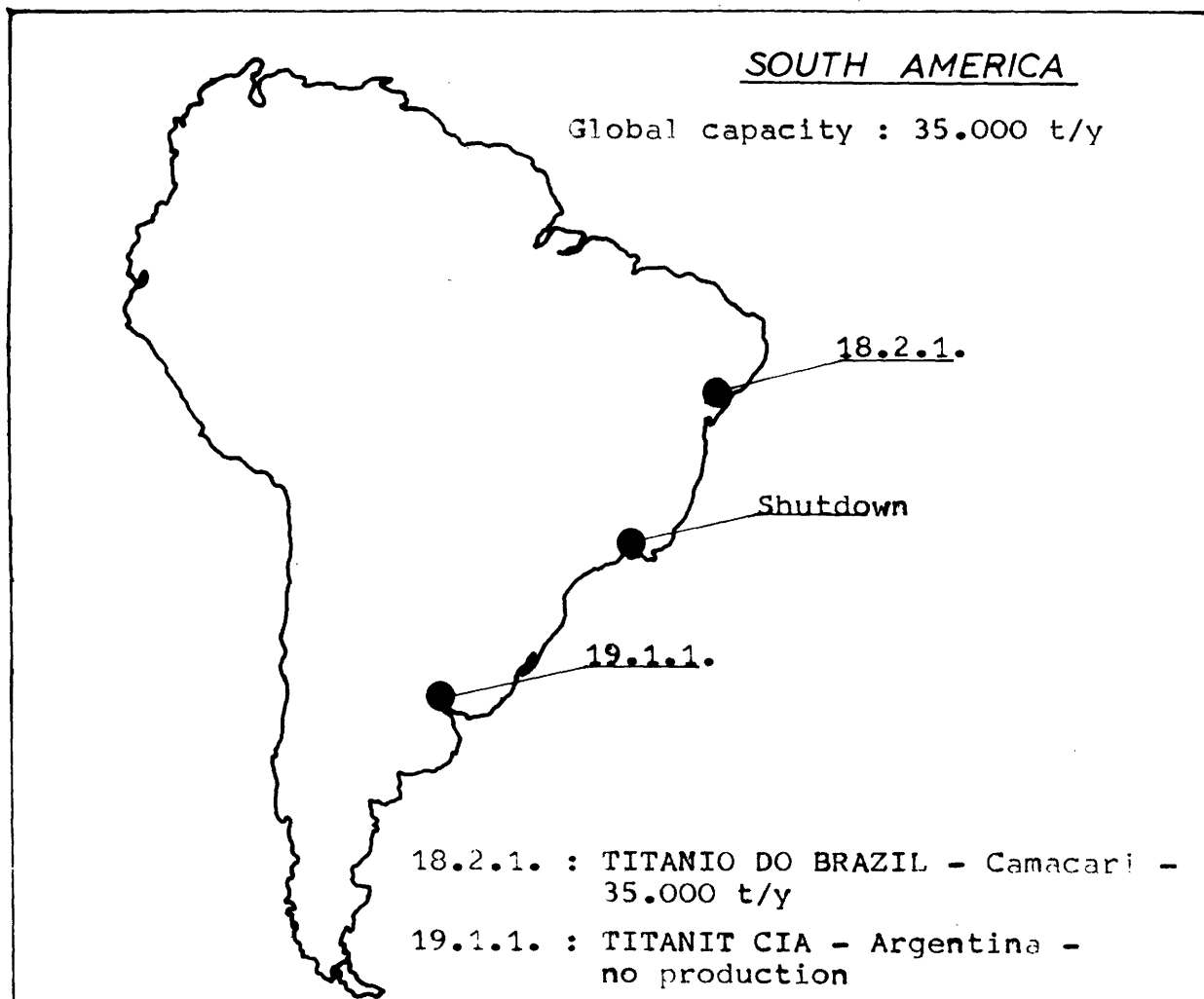
Concentration is carried out in a double effect evaporator based on the DAIDO CHEMICAL ENGINEERING process.

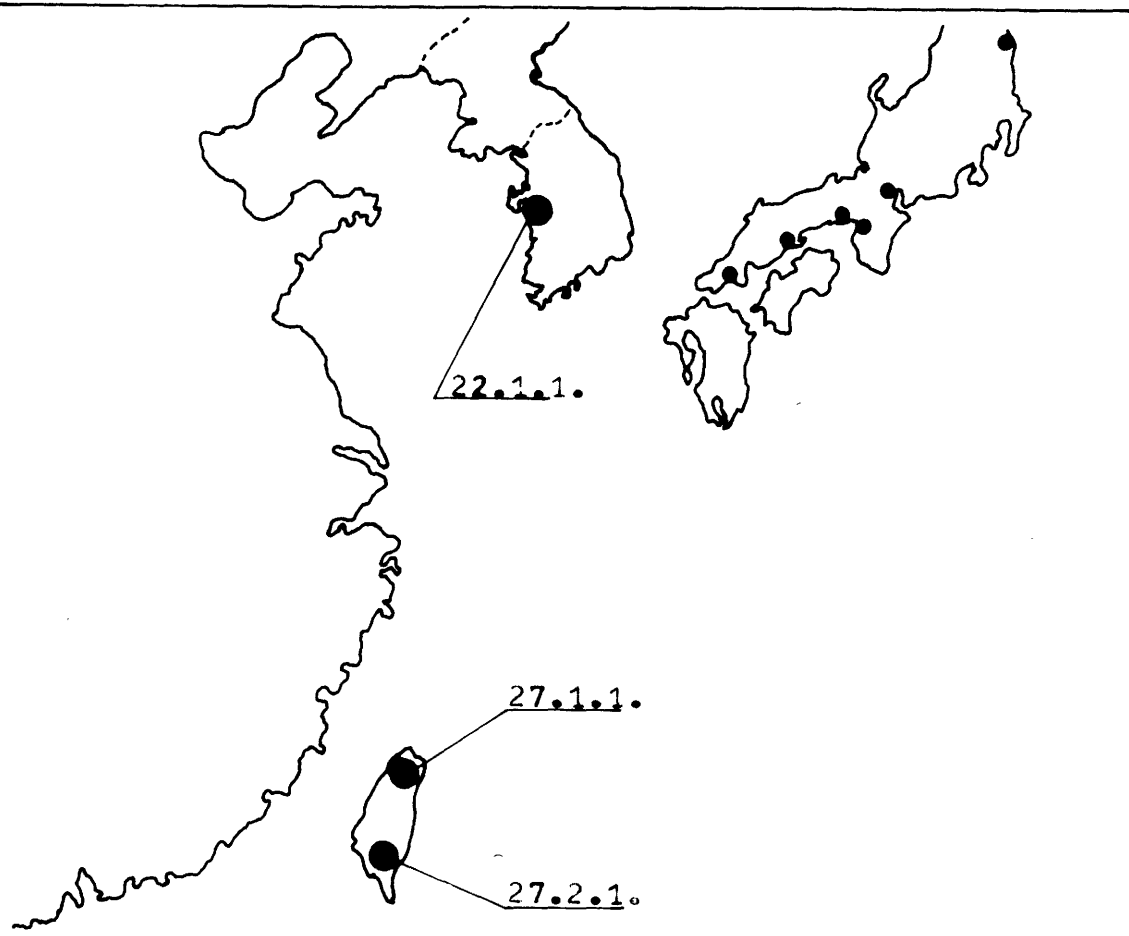
INDIA

Global capacity : 24.000 t/y



23.1.1. : TRAVANCORE TITANIUM PRODUCTS - Trivandrum -
24.000 t/y



SOUTH KOREA AND TAIWANTAIWAN

27.1.1. : CHINA METAL CHEMICAL - Taipei (S) - 6.000 t/y
 27.2.1. : CENTRAL ASIA - Kaohsiung (Finishing) 6.000 t/y

SOUTH-KOREA

22.1.1. : HANKOK TITANIUM - Inch'ôn (S) - 4.000 t/y

ARGENTINA

Ref. : 19.1.1. No in operation

Co. : TITANIT CIA.IND.
PIGMENTOS Y AFINES

Pr. : Sulfate
Loc. : Pilar (Buenos-Air)

KOREA

Ref. : 22.1.1.

Co. : HANKOK TITANIUM

Pr. : Sulfate
Loc. : Inch'ôn (on seaside)
Cap. : 4.000 t/y

INDIA

Ref. : 23.1.1.

Co. : TRAVANCORE TITANIUM PRODUCTS

Pr. : Sulfate
R. Mat. : local Ilmenite
Loc. : Trivandrum (on seaside)
Fil. : 51% State, 25% B.T.P., 24% Private
Cap. : 24.000 t/y (Production 15.000t/y)
Treat. : Wastes are dumped in the sea

Remarks : This company is talking with japanese company
for a process of neutralization

Ref. : 23.2.1.

Co. : KERALA MINERALS AND METALS

Project : Pr. Chloride (Kerr McGee)
Cap. : 28.000 t/y
Completion date : 1980

Ref. : 23.3.1.

Co. : INDIAN RARE EARTHS LIMITED

This company which plans to built a synthetic rutile plant, is also considering the possibility to built a chloride plant within 10 years.

S O U T H A F R I C A

Ref. : 26.1.1.

Co. : SOUTH AFRICAN TITAN PRODUCTS

Pr. : Sulfate (B.T.P. process)
Loc. : Umbogintwini
Fil. : B.T.P. and African explosives and chemicals Ltd.
Cap. : 30.000 t/y

T A I W A N

Ref. : 27.1.1.

Co. : CHINA METAL CHEMICAL

Pr. : Sulfate
Loc. : Taipei
Cap. : 6.000 t/y

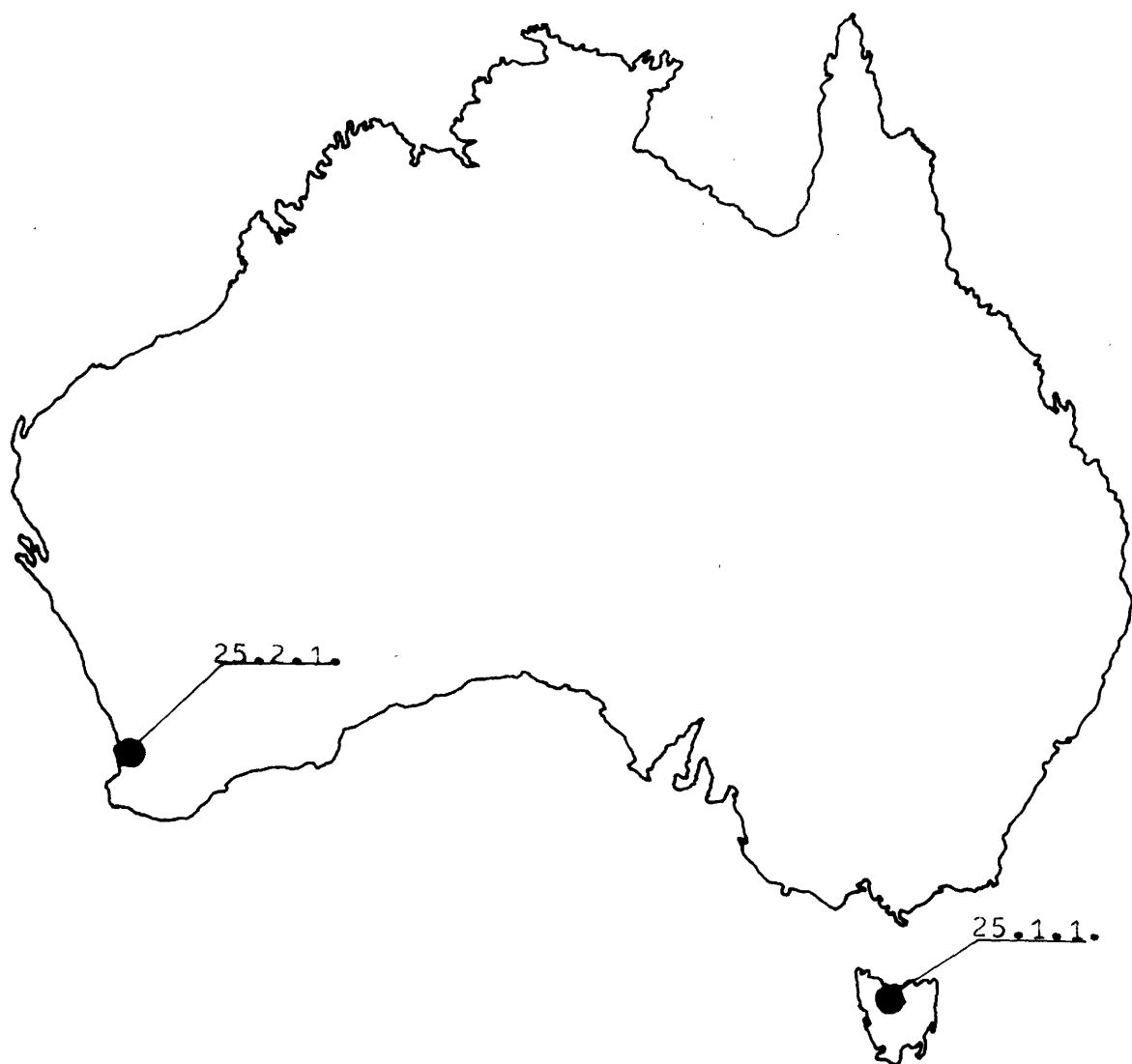
Ref. : 27.2.1.

Co. : CENTRAL ASIA

This plant imports crude TiO_2 from Japan (Iskihara) for finishing steps 6.000 t/y.

AUSTRALIA

Global capacity : 57.000 t/y



- 25.1.1. : AUSTRALIAN TITAN PRODUCTS - Burnie (S)- 27.000 t/y
- 25.2.1. : LAPORTE TITANIUM - Bunbury(S)- 30.000 t/y

A U S T R A L I ARef. : 25.1.1.

Co. : AUSTRALIAN TITAN Products

Pr. : Sulfate (B.T.P.)

R. Mat. : local ilmenite

Loc. : Burnie (on seaside)

Fil. : 100% TIOXIDE ex B.T.P.

Cap. : 27.000 t/y

Treat. : Wastes are dumped in the sea.

Ref. : 25.2.1.

Co. : LAPORTE TITANIUM

Pr. : Sulfate (Laporte)

R. Mat. : Ilmenite from Western titanium

Loc. : Bunbury (on seaside)

Fil. : 100% Laporte

Cap. : 30.000 t/y

Treat. : Wastes are dumped in the sea.

Remarks : This company has an agreement with the state
which has taken the responsibility of the
disposal of the effluents.

SECTION 7

ANNEX

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Down-to-earth solutions ease sludge disposal

Dumping is coming under increasing attack, but processes to solidify industrial wastes promise to overcome some of the objections to landfills. Improved disposal techniques will also help.

Environmental objections to the disposal of raw industrial sludges at U.S. landfill sites are growing. However, many firms in the chemical process industries that now rely on landfills needn't feel down in the dumps. Viable and not too radically different means of getting rid of the residues are emerging.

Incentives for improvements in sludge disposal certainly exist. Accidents as well as potential cases of wastes leaking from rusted-out drums at dump sites pose a severe pollution hazard, argue environmentalists. Concern about such occurrences now rates as a major factor in the limiting of existing, conventional landfill operations, and in the blocking of approvals for new dumps or

even of proposed expansions of present fill sites.

California serves as a good example of what is happening. There are only 11 approved dump sites for hazardous industrial wastes in the entire state. No new fill operations are expected. And some current units are running into problems in getting their permits renewed.

Stricter design and operating criteria for landfill are increasing disapproval for landfill are increasing disposal costs, too, cutting the economic advantage of dumping versus incineration and other alternatives. Moreover, the U.S. Environmental Protection Agency (EPA) is eyeing still more stringent control over dumping (see *Chem. Eng.*, Jan. 20, 1975, pp. 56-58).

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CHEMICAL ENGINEERING, OCTOBER 13, 1975
hardened residues into inert, rock-like materials said to be safe for use in landfill.

The Chemfix system, available for about five years, has been employed in nearly 20 U.S. states, as well as in countries such as the United Kingdom, France and Japan. The route, says the firm, can take care of a variety of inorganic and organic sludges.

Chemfix has successfully treated mercury-contaminated and other heavy-metal-containing wastes, residues from sulfur-dioxide scrubbers, neutralized pickling liquors, API separator sludges, polymer-processing wastes, mud dredgings, as well as

covered over and the ground used as, e.g., a parking lot, or (2) dumped at a landfill tract.

BRITISH TECHNIQUE—Crossford's process, dubbed Sealosafe, differs from the Chemfix method mainly in that it is aimed solely at handling inorganic wastes.

Sealosafe went commercial in September, 1974, when Polymeric Treatments Ltd., which holds the exclusive U.K. license for the route, put onstream a 35,000-ton/yr unit at its Brownhills, Staffordshire, headquarters location.

At Brownhills, individual effluents go through a series of containers fitted with high-speed disintegrators that dissolve and disperse the wastes. At this stage, certain residues, such as those containing arsenic, chromium and cyanides, undergo chemical pretreatment to ensure better handling during subsequent processing. The next step involves treatment with special, undisclosed reagents at atmospheric pressure and ambient temperature to produce a monomer in which pollutants remain trapped by both chemical and physical means.

In slurry form, the monomer then passes to a landfill site—at Brownhills, the dump is an adjacent abandoned marl-clay excavation with enough capacity to take at least 15 years of output from the treatment plant. There, the material polymerizes within three days into a rock-hard solid, according to Polymeric.

The solid is odorless, infestation-proof, noncombustible and nonbiodegradable, says Crossford. It adds that the material also features low permeability, which decreases further with time, good resistance to leaching, and high strength, which builds up during the first year and then remains constant. Dumping sites, notes the firm, can be built upon once they are filled.

UPCOMING RIVALS—Resource Conservation Co. (Seattle, Wash.) and the Systems Group of TRW, Inc. (Redondo Beach, Calif.) are working on sludge-solidification

STOCKPILING

schemes, too.

Resource Conservation has introduced a process called Basic Extractive Sludge Treatment—BEST. This system reportedly produces a bone-dry solid—that is burned, used as fertilizer or feed, or dumped, depending on its nature—and a clear-water effluent from either organic or inorganic sludge via dewatering with a solvent (an aliphatic amine). At the moment, the company is mainly going after the treatment of industrial sludges from sectors such as steelmaking and pulp-and-paper production. Resource Conservation is now operating a 1,500-gal/d. self-contained portable pilot plant for evaluations at sites of potential customers.

In the meantime, in an outgrowth of EPA-sponsored research, TRW has developed at laboratory scale an encapsulation process that the firm says is suited particularly for hazardous wastes such as those containing arsenic, cyanides and pesticides. The company produced its first, small (about 6-in. square) blocks of solid product about a year and a half ago.

The technique centers on introducing small amounts (about 2-3% of the waste charge) of nonbiodegradable, highly cross-linked polymeric material to agglomerate and physically encapsulate the residue. The resulting block is then jacketed with a flexible plastic casing. This acts as a pouch, sealing in odors and keeping out liquids that might leach the wastes. The jacket's flexibility limits danger of its breakage.

TRW foresees production of 2-ft cubes, each weighing about 1,000 lb. These could be stored indefinitely. Claims the firm, or used in landfill operations.

SCRUBBER SLUDGE—Cleaning of utility and other stack gases by scrubbing can produce a lot of sludge. In fact, according to C. N. Iffendi and H. S. Rosenberg of Battelle Memorial Institute (Columbus, Ohio), speaking at AIChE's annual meeting in December, 1974, at Washington, D.C., "... sludge dis-

posal is probably the major problem in the application of lime/limestone scrubbing technology." Conventional landfill usually has been favored for getting rid of the residue, but now IC Conversion Systems Inc. (Philadelphia) and Dravo Corp. (Pittsburgh, Pa.) are boosting solidification processes aimed specifically at tackling scrubber wastes.

IC Conversion Systems has completed at utility plants about a dozen tests of its method, called Poz-O-Tex. The most significant trial, according to the firm, was a run on a scrubber handling one-tenth the offgas from a 1,600-MW power plant. The process reportedly operated successfully on both lime and limestone scrubbing residues.

In the route, sludge is combined with fly ash. Basically, two sets of simultaneous reactions take place—a rapid reaction of sulfates and sulfites with alkali-earth metals to produce a fibrous, gypsum-like material, and a much slower reaction between alumina and silica, lime compounds, and sulfide salts to harden the material until it is like cement.

Product comes out of the Poz-O-Tex process in the form of a wet "sand," which is put into place and compacted. Once it sets, the material is inert, odorless, infestation-proof and noncombustible, says the firm. It adds that the solid can be used as a substrate for road building, as landfill, and possibly as a material for construction.

Meanwhile, Dravo is getting ready for the first fullscale unit of its Calciox process. It features a calcium-based additive that turns sludge from sulfur-dioxide scrubbers into a usable landfill.

Synearth, Pennsylvania Power and Light Co. is installing the pioneer system at its new, 1,760-MW Bruce Mansfield Power Generating Station on the Ohio River near Shippingport.

Taken from *Chemical Engineering*

October 13, 1975

TREATMENTDUMPING (Sea)
BAYER TECHNIQUE**Dünnsäure ins Meer**

Im April 1969 hat Bayer Leverkusen mit der Dünnsäureverbringung in die Nordsee begonnen. Durch diese Maßnahme wird die bei der Pigment- und Farbstoffproduktion abfallende verdünnte ca. 20%ige Schwefelsäure (Dünnsäure) schadlos beseitigt und die Salzfracht des Rheins wesentlich gesenkt.

Die jährlichen Kosten für diese Maßnahmen belaufen sich auf ca. 10 Mio DM. Für die technischen Einrichtungen der Säureverschiffung einschließlich des Schiffbaus waren Investitionen von 37 Mio DM erforderlich.

Das Verfahren der schadlosen Beseitigung von Dünnsäure im Meer wird in anderen Ländern, beispielsweise vor der amerikanischen Ostküste südlich von New York bereits über 20 Jahre, in belgisch-holländischen Küstengewässern seit 1962 angewendet. Dabei sind bisher keine schädigenden Einflüsse auf Meereslebewesen festgestellt worden.

Verdünnung 1:7000

Eine biologische Reinigung der Dünnsäure ist nicht möglich. Auch ihre Neutralisation würde das Problem in keiner Weise lösen, da die dabei entstehenden löslichen und unlöslichen Salze ebenfalls beseitigt und abgelagert werden müßten. Bei einer Neutralisation mit Kalk würden z. B. in Leverkusen über 3000 Tonnen Gipschlamm pro Tag anfallen. Auch eine Rückgewinnung der Schwefelsäure durch Eindampfen ist in Leverkusen weder technisch noch wirtschaftlich sinnvoll. Möglich ist jedoch ihre Verbringung ins Meer, wo sie durch Verdünnung mit Seewasser neutralisiert und damit unschädlich gemacht wird.

Die niederländischen Behörden waren nach eingehenden wissenschaftlichen Studien mit der schadlosen Beseitigung dieser flüssigen Produktionsrückstände im Meer einverstanden. Die Technik des Einleitens der Säure in die See wurde nach umfangreichen Modellversuchen im Waterloopkundig Laboratorium, Delft, erarbeitet. Danach wird die Säure mittels Spezialpumpen in das Kielwasser der mit mindestens 17 Stundenkilometern fahrenden Schiffe abgegeben und durch

Transport

Die Dünnsäure wird in den Betrieben von Bayer und der Titangesellschaft, getrennt von den übrigen Abwässern erfaßt und kontinuierlich durch zwei Sammelleitungen in einen Mischbehälter auf dem Werksgelände gepumpt, dort zu einer Säure mit gleichmäßiger Zusammensetzung vermischt und anschließend in Stapelbehälter am Rhein gefördert. Im Falle von Transportunterbrechungen (z. B. bei Eisgang) können diese Stapelbehälter den Säureanfall von 10 Tagen aufnehmen. Von dort fließt die Dünnsäure durch Abfülleitungen in einem Stollen unter der Bundesstraße EB 8 hindurch zur Verladebrücke. Für den Transport auf dem Rhein bis Rotterdam wurden Schubeinheiten gebaut, die aus sieben Tankleichtern mit einem Fassungsvermögen von je 2200 bis 2500 Tonnen und zwei Schubbooten bestehen. Mehrmals wöchentlich laufen diese modern ausgerüsteten Transportschiffe der Reederei Lehnkering AG, Duisburg, den Rotterdamer Hafen an, wo die Säure nach der Löschung in einem Zwischenlager schließlich in seetüchtige Säure-Tankschiffe überführt und 20 km vor der holländischen Küste völlig gefahrlos für Flora und Fauna im Meer verquirlt wird.

Projekt: Dünnsäureverschiffung

Sammelleitungen	Länge: ca. 5500 m – NW 150, NW 100, NW 80 und NW 65. Werkstoff: Glasfaserverstärkter Kunststoff – Leguval (GfK)/gummiert mit Hartgummi, Qual. H 18.
Mischtank	Fassungsvermögen: 250 m ³ (Durchmesser: 8 m, Höhe: 5,6 m). Werkstoff: Stahl/gummiert mit Baypren, Qual. HW 2 V 18.
Pumpen	4 Kreiselpumpen. Förderleistung: 25 m ³ /h bei ca. 6 atü. Werkstoff: GG 25/gummiert mit Hartgummi, Qual. H 3.
Pumpleitungen	4 Leitungen. Länge: je ca. 1100 m, Durchmesser: 110 mm, Wandstärke: 10 mm. Werkstoff: Polybuten.
Stapeltanks	2 Stapeltanks, Fassungsvermögen 13000 m ³ (Durchmesser: 31 m, Höhe: 17 m) und 7500 m ³ (Durchmesser: 26 m, Höhe: 14,5 m). Werkstoff: Stahl/gummiert mit Baypren, Qual. HW 2 V 18.
Abfülleitungen	2 Leitungen NW 500 in 2 Leitungen NW 200 auslaufend. Länge: je ca. 350 m. Werkstoff: Stahl/gummiert mit Hartgummi, Qual. H 3 bzw. Polybuten.
Verladebrücke	Fachwerkbrücke, Länge: ca. 230 m.
„Leverkusen“ und „Duisburg“	<p>Schubboote Länge: 30 m bzw. 35 m, Breite: 11,2 m bzw. 14 m, Tiefgang: 1,8 m bzw. 1,7 m, Seitenhöhe: 2,5 m bzw. 2,8 m, 2 Antriebsmotore: je 1080 PS bzw. 1600 PS.</p> <p>Tankleichter Länge: 77,5 m, Breite: 11,4 m, Tiefgang: 3,2 m, Seitenhöhe: 3,5 m, Tragfähigkeit: 2200 t oder Länge: 76,5 m, Breite: 11,4 m, Tiefgang: 3,7 m, Seitenhöhe: 4,0 m, Tragfähigkeit: 2470 t, 6 Ladetanks, ausgekleidet mit Baypren, Qual. HW 2 V 18.</p>
„Laumühlen“	Küstenmotortankschiff Länge: 54 m, Breite: 8,4 m, Tiefgang: 3 m, Seitenhöhe: 3,3 m, Tragfähigkeit: 460 t, Antriebsmotor: 500 PS, 4 Ladetanks, ausgekleidet mit Vulcoferran 2231 und Baypren, Qual. HW 2 V 18. Baujahr 1963.
„Käthe H.“	Küstenmotortankschiff Länge: 62 m, Breite: 11 m, Tiefgang: 3,8 m, Seitenhöhe: 4,3 m, Tragfähigkeit: 1140 t, Antriebsmotor: 1000 PS, 6 Ladetanks, ausgekleidet mit Baypren, Qual. HW 2 V 18. Baujahr 1968.
„Rose-Marie S.“	Küstenmotortankschiff Länge: 72 m, Breite: 11,5 m, Tiefgang: 3,6 m, Seitenhöhe: 5,5 m, Tragfähigkeit: 1200 t, Antriebsmotor: 1000 PS, 8 Ladetanks, ausgekleidet mit Baypren, Qual. HW 2 V 18. Baujahr 1972.

Zersetzung von Eisensulfat und Sulfatgemischen (LC)

In den Beizanlagen der Stahlindustrie und in Anlagen zur Erzeugung von Titandioxid fallen große Mengen Eisensulfat und Sulfatgemische an, deren Schwefelinhalt technisch durch thermische Zersetzung der Sulfate rückgewonnen wird. Diese von der Imperial Smelting Corp. Ltd. und den Farbenfabriken Bayer AG zusammen mit Lurgi entwickelten Verfahren sind zugleich ein Beitrag zur Lösung der mit diesen Abfallstoffen verbundenen Abwasserprobleme.

Verfahrensprinzip und Arbeitsweise

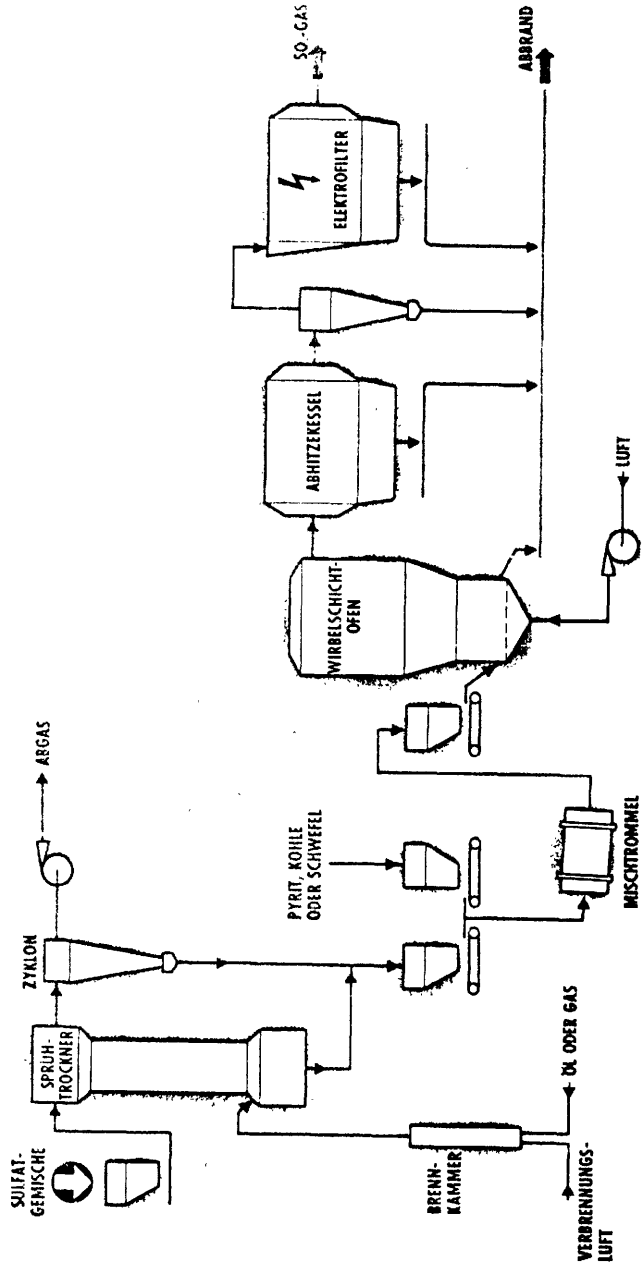
Eisensulfat-Heptahydrat ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$) wird zunächst durch Kalzination (System Lurgi) in das Monohydrat ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) überführt, das anschließend in einem Wirbelschichtofen bei Temperaturen oberhalb 850°C zersetzt wird. Die Zersetzung läuft endotherm, die erforderliche Reaktionswärme wird durch gleichzeitiges Verbrennen von Pyrit, Schwefel, Öl oder Kohle zugeführt. Diese Brennstoffe können entweder einzeln oder kombiniert verwendet werden. Wird Öl oder Schwefel zugefeuert, so fällt der Abbrand als reines Eisenoxid an.

Die heißen Spaltgase werden in einem Abhitzekeßel gekühlt und wie üblich entstaubt. In speziellen Fällen

kann hinter den Abhitzekeßel ein luftgekühlter Wärmeaustauscher geschaltet werden; die aufgeheizte Luft kann zur Kalzination des Heptahydrates bzw. als Wirbelmedium im Wirbelschichtofen verwendet werden. Sulfatgemische und Abfallsäuren werden analog behandelt.

Technische Daten

Durchsatz: 50 bis 300 t/Tag und Einheit
 SO_2 -Gehalt im Abgas: je nach Brennstoff 6 bis 18%
 Restschwefel im Röstgut: je nach Brennstoff 0,5 bis 1,5%
 Zersetzungstemperaturen: 850 bis 950°C



ANNEX 2-2-1

TREATMENT*Ferrous sulfate
roasting**Dorr Oliver process*

A PROCESS for the recovery of iron and acid from ferrous sulphate bearing effluents that will eventually yield sulphuric acid at a cost of approximately £7 per ton, including amortisation and fuel, has been developed by the Dorr-Oliver Co. Ltd., Croydon, Surrey.

The process uses monohydrate cake containing some 7% surface moisture and 1½ to 2¼% free acid obtained by the treatment of spent steel pickle liquor by the Nordac submerged combustion system. In this system the concentration of the spent liquor is raised from 5-12 to 50% at which point the ferrous sulphate settles out as the monohydrate. The monohydrate sludge obtained is de-watered by filtration or centrifugation giving a cake with a water content of between 7 and 3%.

The Dorr-Oliver process involves a two-compartment fluidised bed roaster using the top compartment, and the hot gases from the compartment below, to dry the monohydrate cake, which is converted to a free flowing powder.

Decomposition

Decomposition is carried out at 700°C in the lower compartment where the fuel is blown into a fluid bed together with monohydrate feed, now in powder form. The sulphur dioxide bearing products of combustion pass through an intermediate cyclone where the dust carried over by the other gases is collected and is fed to a products conveyor as is also product discharge from the bed. The hot, clean gases pass upwards to the compartment above where they are used to fluidise another bed and to drive off the surface water in the wet feed. Gases, leaving the system at 300°C, will contain over 14% sulphur dioxide measured on a dry basis.

Apart from the 50% acid recovery from the pickle liquor obtained by Nordacs, the process can be expected to yield 0.465 tons of acid and 0.4275 tons of iron oxide per ton of monohydrate feed.

The economics of the system are attractive. The composition of the waste liquor greatly affects the costs of the Nordac process making it difficult to arrive at a definite cost figure, but, based on a market value of £2 per ton for the monohydrate filter cake, the total cost of the acid production would be in the region of about £7 per ton, when oil is used as the fuel. This cost, which includes fuel, amortisation and labour, is off-set by the resale value of iron oxide which is between £2 and £3 per ton.

Using monohydrate cake with a composition of: $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, 91%; H_2SO_4 , 1.5%; H_2O , 7.5% and with Shell KG heavy fuel for combustion the following

yields could be expected, per ton of monohydrate feed: % SO_2 gas strength, dry basis, 14.525; S.c.f. air, 24,300; Blower abs. power Kwh. 15.175; Oil, lb. 153.75; Oil, gall., 16.2.

Coal, coke breeze or pyrites can be used as fuel, in the place of oil, but coal can give rise to stack problems, and all three would entail rise in capital and power costs for their preparation as ground feed.

Designs are so far available to handle 1, 1½, 2 and 2½ tons per hour of the filter cake; larger capacities in single units are possible but, for flexibility, it is preferable to operate multiple units in parallel.

The liquor obtained from steel plate pickling is the ideal, as the monohydrate is easily obtained. Such a monohydrate was used by the Dorr-Oliver Co. in their test runs at Dorking. It came from Port Talbot, and is the Lurgi source of monohydrate supply.

It is not quite so easy to obtain a monohydrate of suitable crystal size from titanium liquors because of the way the septahydrate settles out at a very early stage. However, Nordac's have succeeded in producing a cake which Dorr-Oliver have been able to decompose in their Dorking laboratories. Also British Titan Products have patented a process whereby the septahydrate may be converted to free flowing monohydrate powder.

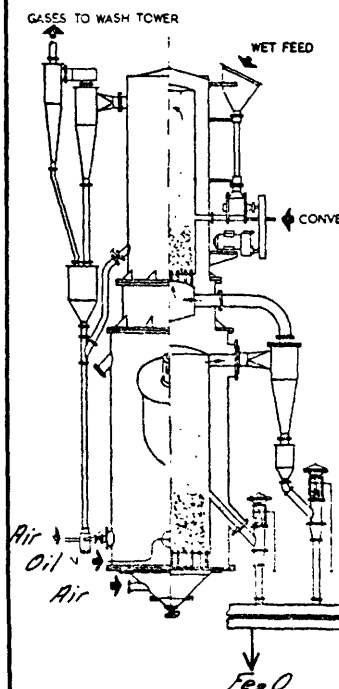
Dorr-Oliver 16 ft. diameter fluid bed roasters have been in operation for a year at the Pyewipe Works of British Titan Products Ltd. In this instance the monohydrate is obtained from Kestner spray dryers, which are fed with the slurry from the by-product liquor of titanium dioxide preparation from ilmenite. Acid production of up to 70 tons per day per reactor is being achieved and the oxide, containing an average of 1% sulphur, is being sold as blast furnace feed. Chemical Construction (G.B.) Ltd., were the main contractors.

Other Processes

There are several other systems for the recovery of the monohydrate, such as the autoxidation, the Ruthner and the Zahn process, which all employ evaporation of the pickle liquor in the first stage to obtain the monohydrate. Iron oxide recovered by the Ruthner process is re-salable to steel mills and, according to U.S. figures given in an article 'Evaluation of waste pickle liquor treatment' by T. F. Barnhart, the process cost per of acid, offset by the sale of oxide at \$8 per ton, is in the region of \$35.40 to \$31.80 per ton according to plant size.

Other methods include the Belle Fons process, which operates under a vacuum, but which has so far only reached the pilot plant stage, and an electro-dialysis process.

A Dorr-Oliver dryer/roaster. Such units are supplied with a blower capable of passing, for example, 900 s.c.f.m. against a back pressure of 5.5 p.s.i.g., all instrumentation which would make operation virtually automatic, supporting steel work with platforms and ladders and necessary refractory and lagging



D.O.B.V.

27 January 1975

FERROUS-SULFATE DECOMPOSITION-PLANTS

1. Client : British Titan Products
 Plant-location: Grimsby/England
 Size : 3 units for handling totally 340 MTPD of ferrous sulfates
 Start-up : 1959
 Auxiliary fuel: Pulverized coal
 Note : Units were built for the prime purpose of recovering the sulfur as SO_2 -gas for sulfuric-acid production. After some ten years of operation, plants have been shut down because of severe drop of sulfur-prices.

2. Client : Officine de Porto Torres
 Plant-location: Porto Torres/Sardinia
 Size : 1 unit for handling totally 580 MTPD of ferrous sulfates and pyrites
 Start-up : 1970
 Auxiliary fuel: Pyrites
 Note : Also this plant was built to recover sulfur, but shortly after initial operation it was converted for burning elemental sulfur.

3. Client : Montedison
 Plant-location: Spinetta-Marengo/Italy
 Size : 1 unit for handling 140 MTPD of ferrous sulfates
 Start-up : 1971
 Auxiliary fuel: Pyrites and/or fuel-oil

4. Client : Montedison
 Plant-location: Scarlino-Follonica/Italy
 Size : 1 unit for handling 600 MTPD of ferrous sulfates
 Start-up : 1976 (expected)
 Auxiliary fuel: Natural gas

TREATMENT EUTECO PROCESS FOR COPPERAS TREATMENT

Clayey soil conditioners from ferrous sulphate wastes

FERROUS sulphate, a highly polluting by-product from sulphate route titanium dioxide plants, represents a major disposal problem. Producers of titanium dioxide are subject to heavy pressure to stop ferrous sulphate waste dumping at sea.

Euteco has developed a new process for ferrous sulphate treatment which not only provides a solution to the disposal problem but also transforms a waste by-product into a valuable material. The process produces clayey soil conditioners that can significantly increase the productivity of low-fertility soils.

Description of the process

The Euteco process originated from experiments demonstrating that some ferric salts modified the structure of clayey alkaline soils, conferring porosity and permeability and therefore enhancing their fertility.

It uses very simple equipment and economical operations and is covered by patents and patent applications in Italy and in the main countries of the world.

Ferrous sulphate heptahydrate from the crystallization step of the TiO_2 plant is dry mixed with calcareous material or hydrated lime, with which it reacts to form ferrous hydroxide and calcium carbonate. The product obtained is then processed in a stream of hot air to completely oxidize the ferrous hydroxide to ferric hydroxide. The mixture is also dried in this step.

High-strength sulphuric acid is then added to the dry product until all the ferric hydroxide has been converted to ferric sulphate. The material is finally cooled and classified by screening and oversize crushing in order to get the suitable particle size (less than 2 mm.).

Properties of the product

The product, which consists primarily of ferric and calcium sulphates, has been extensively characterized in the laboratory and by agricultural tests. Its average composition is given in *Table 1*. It is produced in the form of yellowish grey coloured granules and can be packed, transported and stored just like any other fertilizer.

Modifications of the micro- and macrostructure of several treated soil samples and the resulting changes in their physico-mechanical properties were studied in the laboratory. It was observed that the product is effective on alkaline soil. Further studies therefore focused on clayey alkaline soils which, because of their particularly compact structure, hinder the development of microflora and retard plant growth.

It was seen that a ferric conditioner treatment lowers the compactness of such soils and increases their porosity and permeability to air and water—two properties that are prerequisites for fertility. In fact the ferric ions act as a flocculant on the clayey colloid particles by forming granular particles through dehydration of the gels. The effect is progressive and appears to be irreversible.

Table 1: Average composition of ferric conditioner (wt/%)

Ferric sulphate	43.0
Calcium sulphate	34.0
Magnesium sulphate	2.5
Ferric oxide	2.5
Free sulphuric acid	3.0
Water	13.0
Others	2.0

Field and agricultural tests

Extensive field tests have been performed to evaluate the effects of the conditioner on clayey soils and a number of useful modifications were observed. These include:

- Increased porosity and permeability to air and water;
- Increased water reserves available to plants;
- Reduced hardness;
- Reduced cracking;
- Reduced soil compacting due to rain, irrigation and machinery;
- Increased resistance to erosion.

Agricultural tests on trees and a variety of crops have been performed on low-fertility calcareous clayey soils in several locations in Italy and abroad. The crops included: maize, wheat, barley, sorghum, darnel, tomatoes and grapes.

Depending on the type of treatment, the original characteristics of the soil, and the type of plants studied, crop yields have been increased as much as 200 per cent. Cereals, forage crops, second crops, legumes and flowers responded particularly well to treatment with the ferric conditioner. The quantity of conditioner used ranged from 2.5 to 10 ton per hectare, depending on the depth of the treatment and the nature of the soil.

Dynamometric measurements showed that significant energy savings were also obtained because the improved properties of the soil make it easier to work. It can therefore be concluded that Euteco has succeeded in transforming a harmful waste by-product into a valuable and economical soil modifier suitable for the recovery of land for agriculture, the improvement of low-yielding land, and afforestation.

TREATMENT

COPPERAS VALORIZATION
EUTECO PROCESS

Consumption and labor

a) Raw materials (basis 1 ton of product)

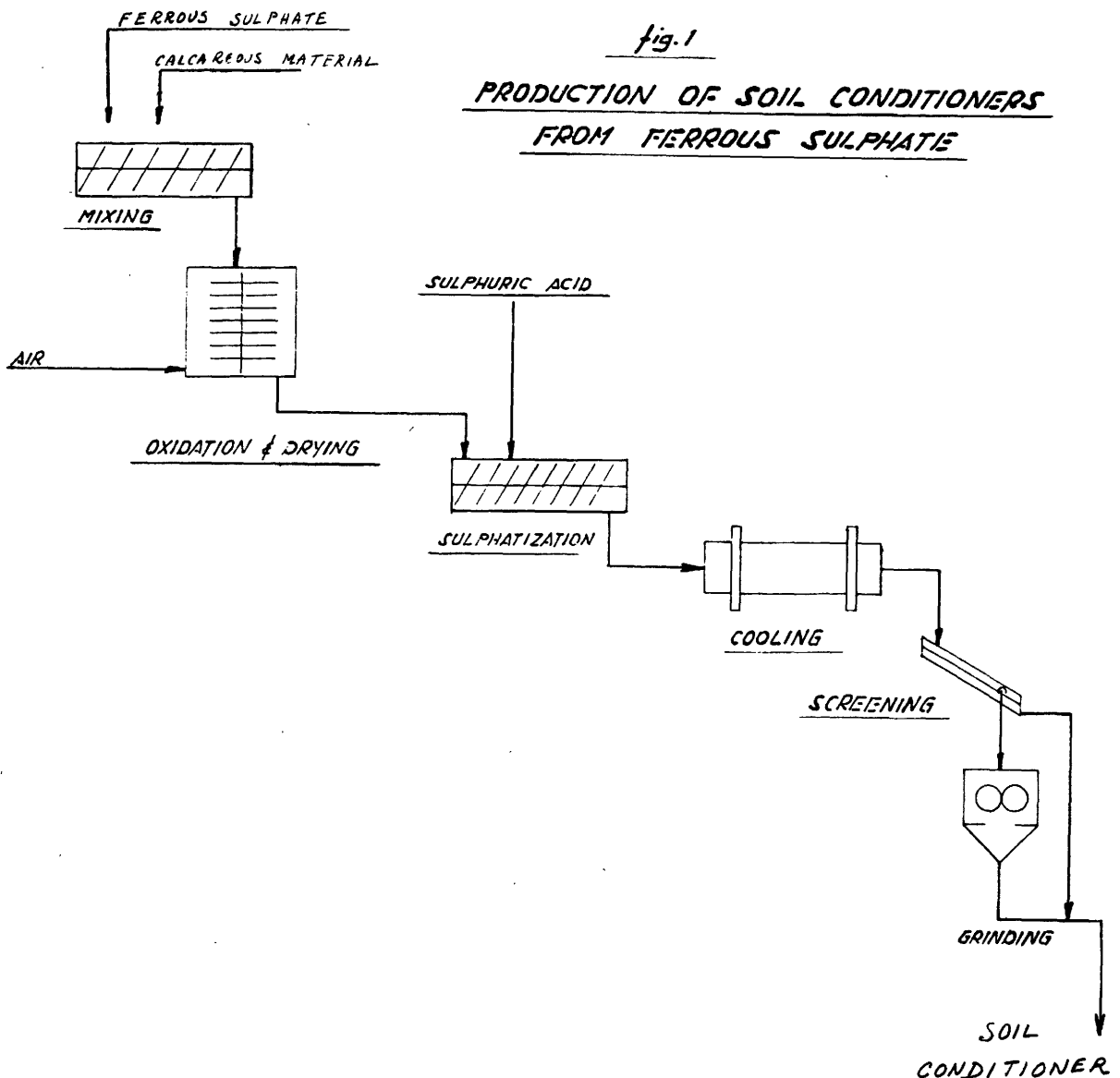
- Ferrous sulphate 760 kg
- Calcareous material 260 kg
- Sulphuric acid (100%) 345 kg

b) Utilities (basis 1 ton of product)

- Electric power 18 kWh
- Fuel 20 kg

c) Labour (basis 600 MT/D plant)

3 men/shift



TREATMENT

ISHIHARA SANGYO KAISHA

(taken from an advertising brochure)

There are various kinds of industrial waste liquors containing sulphuric acid. Among them, it is considered that the waste acid liquor resulting from steel pickling and titanium dioxide manufacture is largest in quantity as a single waste of this character.

For many years, these waste acid liquors have posed a disposal problem, and in order to prevent stream pollution caused by their discharge, ordinarily they are treated with lime or some other alkaline agents. However, this is a costly procedure because no products of value are obtained.

The most important aspects of treatment of waste acid liquor are the cost of doing the job and the value of products therefrom.

Ishihara Sangyo Kaisha, Ltd., the top manufacturer of titanium dioxide pigment in Japan, has developed an economical treatment process of such waste acid liquor containing free sulphuric acid, ferrous sulphate and some other sulphates of metals as discharged from steel pickling or titanium dioxide manufacture, and constructed a plant in Yokkaichi, Japan, which commenced its operation in September, 1961.

The process pertains to the treatment of the waste acid liquor with ammonia, thereby recovering the metals contained therein as useful compounds and the total sulphate radical as ammonium sulphate. The features of the process are to form the filterable precipitate of metal hydroxides by special technique, to remove iron as hydrated iron oxide by air oxidation, and to evaporate the remaining liquor crystallizing out magnesium ammonium sulphate and ammonium sulphate. Another feature of the process is to use only ammonia recovering useful products from the waste acid liquor.

Component in waste acid liquor Products recovered

Total sulphate radical	Ammonium sulphate
Iron when contained	Hydrated iron oxide
Magnesium (if exists)	Magnesium ammonium sulphate
Titanium (if exists)	Hydrated titanium oxide
Aluminium (if exists)	Ammonium alum
Vanadium (if exists)	Ammonium metavanadate

Ammonium sulphate

Ammonium sulphate continues to have the largest demand as nitrogen fertilizer. Ammonium sulphate obtained by this process contains more than 20.5% of nitrogen and is by no means inferior to other synthesized grade. The product is also endowed with large crystalline particles and is easy to handle.

Magnesium ammonium sulphate

As a fertilizer, magnesium sulphate, magnesium sulphate and ammonium sulphate are commonly used. Magnesium ammonium sulphate is a valuable fertilizer because of its high water solubility and its fertilizing effect in soil for a longer period than magnesium sulphate because of its low solubility in water.

Especially, it is useful for the soil lacking in magnesium and for orchards. It can also be used to produce compound fertilizer containing water soluble magnesium.

Hydrated titanium oxide

As it is readily soluble in sulphuric acid, it may be charged into the titanium dioxide manufacturing process. After calcining it may be chlorinated into titanium tetrachloride, which is converted to titanium dioxide in chloride process.

Hydrated iron oxide

With less impurities and accordingly being high grade, it is far superior to pyrite cinder as raw material for the manufacture of iron.

Depending upon operational conditions, various crystal systems of hydrated iron oxide are obtainable. It can be made into various kinds of pigments such as yellow, red, brown and black. Or, it may also be used for ferrite or high purity iron by raising its purity.

Ammonium alum

It may be used for treatment of sewage, industrial water or city water as clarifying and precipitating agent and for the paper industry instead of aluminium sulphate. It is also used as a clarifying agent mordant in dyeing and an ingredient in battery powder.

Ammonium metavanadate

It is valuable as raw material for the oxidizing catalyst in the production of sulphuric acid, phthalic anhydride, maleic anhydride and other organic acids. It may be used as colorant in ceramic industry, and may be used also as raw material for ferrovanadium alloy.

When the waste acid liquor containing free sulphuric acid and ferrous sulphate is subjected to neutralization with ammonia under an oxidizing condition, the iron is precipitated in the form of readily filterable crystalline hydrated oxide, which may be then separated by filtration. However, when aluminium or titanium sulphate is present in the waste acid liquor, it is co-precipitated as colloidal hydroxide with hydrated iron oxide under neutralization with ammonia, and it is difficult to separate such co-precipitate from the liquor by filtration. Therefore, such undesirable components as aluminium, titanium, etc. must be removed previously.

1. Neutralization Step

When the waste acid liquor is added with ammonia, aluminium, titanium, vanadium, etc. is precipitated as hydroxide of a lower pH value than that at which iron is precipitated.

In this step, the waste acid liquor is added with ammonia continuously under precise control of pH value, and the undesirable components such as aluminium, titanium, etc. are precipitated as hydroxides, which are grown large in their particle size by the special technique and separated from the liquor by filtration leaving iron in the liquor. The cake of hydroxides separated is treated in by-process.

When a waste acid liquor to be treated contains little or no aluminium, etc., this step may be omitted.

2. Oxidation Step

The liquor, from which aluminium, titanium, vanadium, etc., have been removed, is an ammonium sulphates solution containing sulphate of iron and in some cases magnesium, etc. The ferrous sulphate is oxidized by introducing air in the liquor and at the same time adding ammonia to be precipitated as hydrated iron oxide of crystalline. The precipitate of hydrated iron oxide increases particle size by controlling the air flow and the pH value of the liquor and is separated readily from the liquor by filtration. The filter cake of hydrated iron is washed, while the filtrate is fed into evaporator in the subsequent step.

3. Evaporation and Crystallization Step

The liquor, from which the hydrated iron oxide has been removed, is an ammonium sulphate solution, in some cases containing magnesium sulphate. The liquor is fed into the third effect of the triple effect evaporator, in which it is concentrated by evaporation. The concentrated liquor is led to the cooler, in which the magnesium sulphate is crystallized out from the liquor.

The mother liquor, from which the magnesium ammonium sulphate has been separated, is fed to the first effect and then sent to the second effect to be evaporated further. In the second effect ammonium sulphate magma is formed, and is led to a centrifuge, in which the ammonium sulphate crystal is separated from the mother liquor. The mother liquor is returned to the first effect.

PLANT CAPACITY

Plants with any capacity of producing ammonium sulphate may be constructed depending upon the quantities of waste acid liquor to be treated. The table below shows the capacities of producing ammonium sulphate in relation to the quantities of waste acid liquors.

Titanium dioxide waste acid liquor	Capacity of producing ammonium sulphate	Quantity of waste acid liquor of standard composition*
2,500 tons/M	2,500 tons/M	10 m ³ /hr.
1,500 tons/M	1,500 tons/M	9 m ³ /hr.

Ref. * Titanium dioxide waste acid liquor.
Total H₂SO₄: 320 g/l.
* Waste pickle liquor.
Total H₂SO₄: 200 g/l.

OPERATION RESULTS

A. Titanium dioxide waste acid liquor

Following data have been obtained based on one year operation.
Waste acid liquor treated (T₂O₅): 320 g/l. 6500 m³/M
Ammonia required 680 tons/M

Utilities (based on ton of ammonium sulphate)

Electric power	100 KWH
Fuel oil for drying ammonium sulphate	6L.
Steam	1.2 tons
Sea water	45 "
Process water	15 "

PLANT SET UP

This process is divided into two processes, main and by-process. The main process consists of three steps namely, neutralization, oxidation and evaporation. The by-process is applied for recovering by-products from hydroxide cake separated in neutralization step and may be omitted if the waste acid liquor to be treated contains little or no aluminium, titanium or other metals except iron.

The principal equipment as well as waste acid storage tank, ammonia storage tank and ammonia vaporizer are erected outdoors. Filters to operate concentrically by controlling pH, temperature, flow of fluid, etc., with various meters.

Labour 2.6 man-hr
Operation rate above 90%
Ammonia recovery above 95%

Products
Ammonium sulphate (NH₄-N: 20.5-21.0%) 2,500 tons/M
Magnesium ammonium sulphate (NH₄-N: 7-8%, W-MgO: 10-11%) 300 "
Hydrated iron oxide (wet base, H₂O: below 25%) 300 tons/M
Hydrated titanium oxide (TiO₂ base) 32 "
Ammonium metavanadate 5 "

B. Waste pickle liquor

Following data are expected.
Waste pickle liquor treated (T₂O₅): 200g/l. 5,700m³/M

COMPOSITION OF WASTE ACID LIQUOR

The titanium dioxide waste acid liquor is influenced in quantity and composition by the titanium dioxide manufacturing process and titanium are used, while the waste pickle liquor is invariable in composition generally.

The ranges of the compositions of these waste acid liquors are shown below.

Titanium dioxide waste acid liquor (g/l)						
T ₂ O ₅	F ₂ SO ₄	Fe	Al	Ti	Mg	V Cr.
200	100	20	0.5	0.5	0.5	0.2 0.1
—500	—400	—50	—10	—10	—10	—2 —2

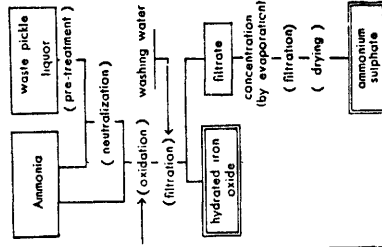
Ammonia required 415 tons/M
Pretreatment agent for removing inhibitor 12 tons/M
Utilities (based on ton of ammonium sulphate)

Electric power	90 KWH
Fuel oil	6L.
Steam	1.5 tons
Sea water	45 "
Process water	15 "
Labour	1.55 man-hr.
Operation rate	above 90%
Ammonia recovery	above 95%
Products	
Ammonium sulphate (NH ₄ -N: 20.8-21.0%)	1,500 tons/M
Hydrated iron oxide (wet base, H ₂ O: below 25%)	500 tons/M

Waste pickle liquor (g/l)

T ₂ O ₅	F ₂ SO ₄	Fe
130—300	70—100	50—90

In titanium dioxide manufacturing process, a concentrated waste acid liquor is obtained by filtration of hydrolysed liquor, and a dilute waste acid liquor is obtained by washing hydrated titanium oxide cake separated from the concentrated waste acid liquor. This dilute liquor may be mixed with the concentrated one. The quantitative limit of mixing them for the treatment by this process should be decided depending upon the necessity of their treatment and the profitability of enterprise.



TREATMENT WASTE ACID NEUTRALIZATION

June 16, 1953

A. L. NUGEY

2,642,334

METHOD OF NEUTRALIZING INDUSTRIAL WASTE

Filed Sept. 20, 1947

Fig. 1.

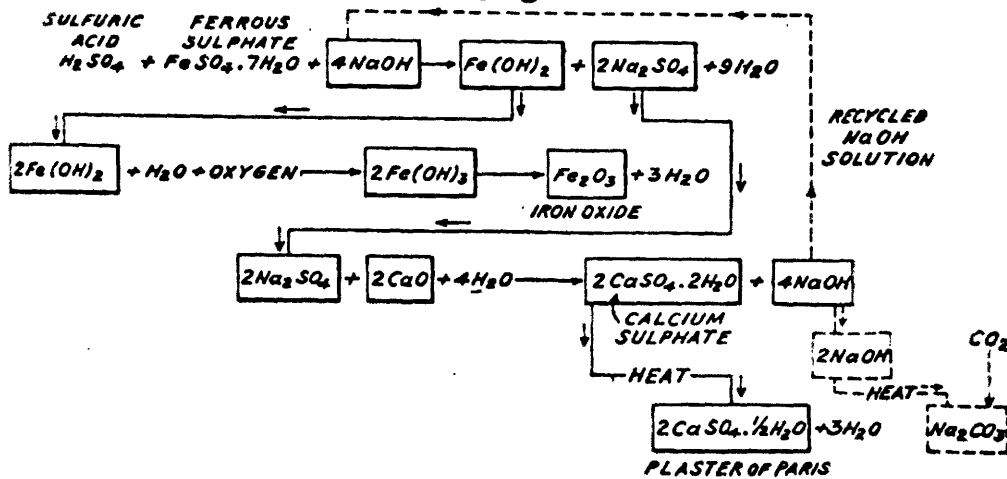
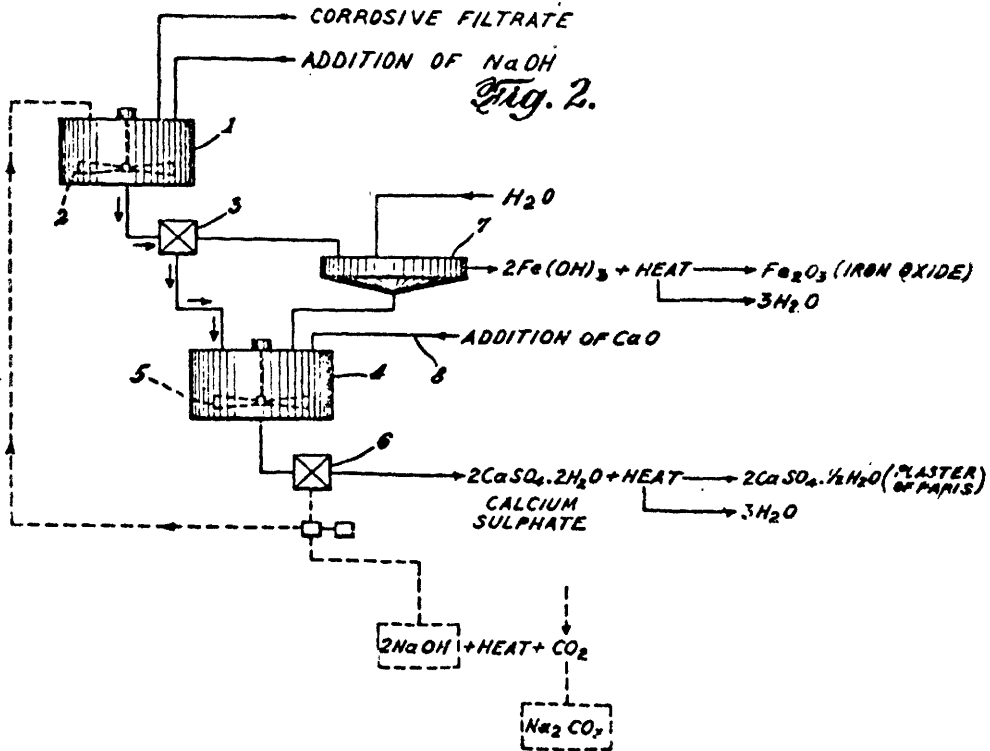


Fig. 2.



INVENTOR.
Anthony L. Nughey.
BY
William F. Nickel
ATTORNEY.

TREATMENT

WASTE ACID TREATMENT JAPAN SOLEX Co PROCESS

1. Introduction

Since Japan imports smelts and processes high-grade raw materials to produce nonferrous metals, to be exported, cost reduction is necessary in these steps. Specifically smelting cost is desired to be cut by mass production, and by the selective treatment of high-grade ores. Unlike other countries of the world, where metals are separated and purified by solvent extraction developed as a hydrometallurgical process, Japan today seldom yields them by the complex, troublesome treatment of low-grade material or by recovery from abundant industrial wastes. The solvent extraction method, therefore, has come to be only used in limited areas.

In 1966, Japan Solex Co., Ltd., being aware of the necessity for energy saving, pollution prevention and resource recovery, focussed attention on the solvent extraction technique, and started cooperation with the metal extraction research laboratory of Prof. Nishimura, Kansai University, Osaka. Solex and the laboratory, under a joint study in 1971, judged the technique to be efficient and promising after continuously running a pilot plant for a month to recover chromic acid from spent acid discharged out of the hard chromium plating process. Although the result was published in newspapers, hardly anyone seemed to become interested in it. Thus this production method for metals has not been commercialized to this day.

After the oil crisis of 1973, pollution prevention in parallel with resource recovery became a serious industrial and social concern. Secondary pollution, particularly with mercury and hexa-valent chromium contained in industrial wastes, caused a shock to society. Industry, therefore, tends to use more expensive energy and raw material resources. In the near future good quality resources especially of various raw materials will be exhausted. The solvent extraction technique, by itself or in combination with other technology, will help much to solve these problems. The licensing and technological export of this patented process are made through a governmental channel, the Research & Development Cooperation of Japan (JRDO).

2. Application in manufacturing process of titanium dioxide using H₂SO₄

In the conventional production of TiO₂ using H₂SO₄ required 98% H₂SO₄ per 1 ton of TiO₂ product amounts to 3.5 to 4.0 tons. About 40% of used H₂SO₄ is discarded as a waste acid containing 300-350 g/l of H₂SO₄, 30-35 g/l of Fe and 7 g/l of TiO₂ and residual 60% is by-produced as FeSO₄·7H₂O. Hitherto, the economical treatment of these FeSO₄·H₂O and waste acids by-produced in abundance has not been found. They have been allowed to be discarded untreated, and have given rise to serious pollution problems, hampering TiO production using H₂SO₄.

As shown in a separate flowsheet, our solvent extraction technique adds 350g of a solution containing Fe²⁺, Ti⁴⁺, and TH₂SO₄ to a liter of spent acid to be treated, introduces the mixture to an anode compartment separated with membrane from a cathode compartment which is filled with a solution containing Fe³⁺, and forms an oxidation-reduction electric cell by wiring electrodes immersed in the two compartments. Introducing the solutions to both compartment in multistage counterflow will help oxidize Fe²⁺ in spent acid to Fe³⁺. The liquor under treatment is then sent to the extraction step where acid gets regenerated after Fe³⁺ and Ti⁴⁺ have been extracted in an organic solvent containing dialkylphosphoric acid like D2EHPA. If H₂SO₄ concentration drops below 400g/liter, by-produced FeSO₄ is dissolved to oxidize Fe³⁺ further to raise H₂SO₄ concentration to about 450g/liter by repeating extraction. Then the concentrated liquor is introduced to an enriching device to obtain 80-90 per cent H₂SO₄, which is then returned to the resolving of Ti raw material.

Meanwhile, Fe³⁺ ions dissolved in the organic solvent are made to contact 150-200g/liter of HCl to be extracted from the solvent. Then the remaining liquor is made to contact a (NH₄)₂CO₃ solution to remove Ti⁴⁺ ions in the form of Ti(OH)₄ as a sediment in water. The residual solution, in the form of ammonium compound, is now made to contact part of the recovered H₂SO₄ to be converted to a hydrogen compound and to recover by-produced (NH₄)₂SO₄.

The 150-200g/liter HCl used to separate Fe³⁺ ions is diverted to contact an organic solution containing TBP, for forming a complex of iron chloride with TBP to be separated from V ions.

The HCl solution, having fewer T.Cl- ions after the above extraction forming HFeCl₄, is allowed to the middle compartment of the membrane electrolysis cell, where the solution receives H ions from the anode compartment and Cl ions from the cathode compartment to make a more concentrated HCl solution to be recycled to the Fe³⁺ separation from the organic solvent.

Fe³⁺Cl ions extracted in the form of HFeCl₄, on the other hand, is separated from the solvent containing the HFeCl₄ in contact with catholyte. The regenerated solution is recycled to extract HFeCl₄.

Since the catholyte now contains Fe²⁺ and Fe³⁺ ions, it may be employed to form an oxidation-reduction cell in combination with spent acid having Fe²⁺. Thus the two varieties of Fe ions exchange ionic valencies, helping reduce energy to be supplied from external sources to carry out electrolysis.

In the meantime, to the cathode compartment is supplied an electrolyte controlled to contain no heavy metal ions but Fe ions to obtain electrolytic iron efficiently.

Manufacturing equipment using this method can be constructed side by side with existing facilities without modification of the conventional TiO₂ production process and change of its control system; the adaptability to practical use is a significant feature of the method. A closed system, effective for solution of public pollution problems, can be formed with a function to recover concentrated acid easily by extracting ions of heavy metals from discarded waste acids or by-produced FeSO₄.

Economic improvements or a selection of raw material containing Ti can be facilitated by fractional recovery of various metal ions as high purity metal salts or oxides. This method can be applied in treatment of FeSO₄ by-produced in iron and steel making.

Taken from
Chemical
Economy
and
Engl. Review
1976

Table 1 Cost of construction (capacity 3,000 TiO₂/month)

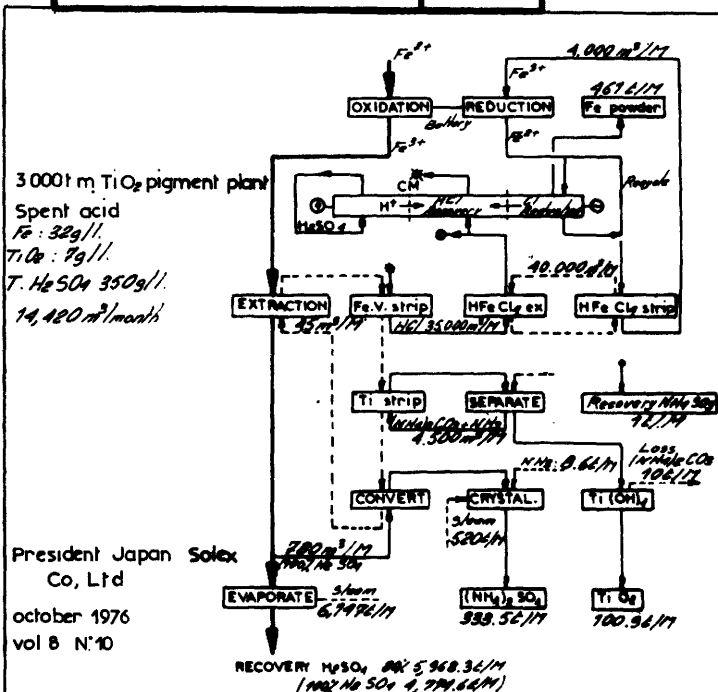
Solvent extraction process	Y 448,000,000
H ₂ SO ₄ concentration process	Y 374,000,000
(NH ₄) ₂ SO ₄ crystallization process	Y 246,000,000
HCl recovery process	Y 687,000,000
Total	Y 1,755,000,000

(a) Utility			
Solvent (A)	400 kg/month	1,500	Y 600,000
Solvent (B)	750 kg/month	1,000	Y 750,000
(NH ₄) ₂ CO ₃	10 t/month	50,000	Y 500,000
35% HCl	34.2 t/month	15,000	Y 513,000
NH ₃	94.6 t/month	65,000	Y 6,149,000
Ca(OH) ₂	13.0 t/month	107,000	Y 130,000
Fuel	30 kl/month	27,000	Y 810,000
Steam	6,667 t/month	2,500	Y 16,667,500
Power	1,688 x 10 ³ kWh	8	Y 13,504,000
Total			Y 39,623,500

(b) Capital investment amortization and interest	Y 21,937,000
(c) Maintenance cost	Y 3,947,000
(d) Labor cost 10 x 30 /month	Y 4,500,000
Total	Y 70,007,500

(e) Recovery			
H ₂ SO ₄ (80%)	5,968.3 t/month	6,000	Y 35,809,800
Fe powder	461 t/month	50,000	Y 23,050,000
TiO ₂	100.9 t/month	200,000	Y 20,180,000
NH ₄ VO ₃	1 t/month	500,000	Y 500,000
(NH ₄) ₂ SO ₄	333.3 t/month	15,000	Y 5,002,500
Total			Y 84,542,300

(f) Balance	
84,542,300 - 70,007,500 =	Y 14,534,800/month



TREATMENT

SULFURIC ACID RECYCLING

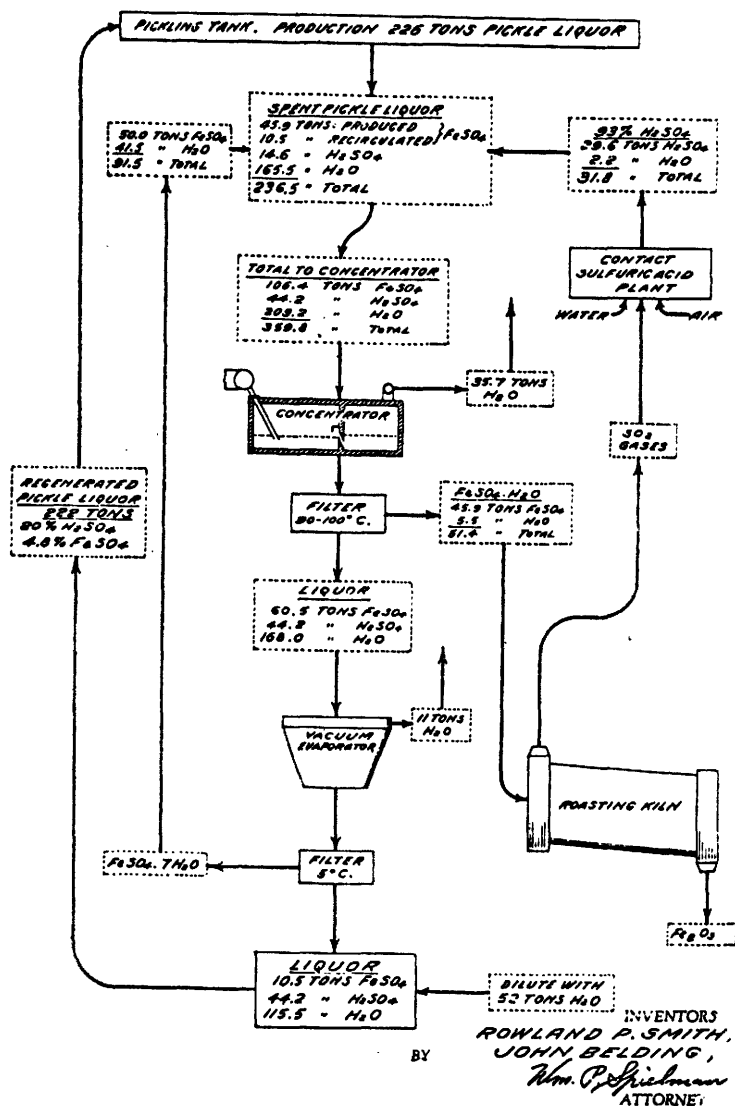
Dec. 26, 1939.

R. P. SMITH ET AL

2,185,095

REGENERATION OF WASTE FERROUS SULPHATE LIQUOR

Filed Oct. 29, 1938



Spangler² described a commercial method comprising the contact process for recovering the sulfuric acid values from spent liquors from titanium pigment manufacture. Such solutions normally contain 18 to 25 per cent sulfuric acid, 10 to 18 per cent ferrous sulfate, and small amounts of titanium sulfate. The free acid was first neutralized with iron oxide, which was obtained from a subsequent step of the process, and the resulting solution was evaporated to recover anhydrous iron sulfate. Both neutralization and evaporation were safely carried out in one rotary kiln heated internally by combustion of gases. The iron sulfate residue was then decomposed in a rotary roaster to produce sulfur dioxide gas of the proper concentration for subsequent conversion in a contact acid plant, and ferric oxide cinder, a part of which was returned for the neutralization of additional batches of waste liquor. After purification, the sulfur dioxide was converted to sulfuric acid of any desired strength in a modified form of the standard Chemico contact-acid plant using vanadium catalyst. This procedure, using dehydrated iron sulfate, was similar to the conventional contact process employing pyrite or sulfur, except that a heating and reducing agent was added to the raw material. Low-grade fuel or pulverized coal proved quite satisfactory, and pyrite was mixed with the sulfate residue, thus supplying part of the heat required and at the same time producing sulfur dioxide to enrich the roaster gases. A plant of this type was constructed for the National Lead Company, Titanium Division, in 1934.

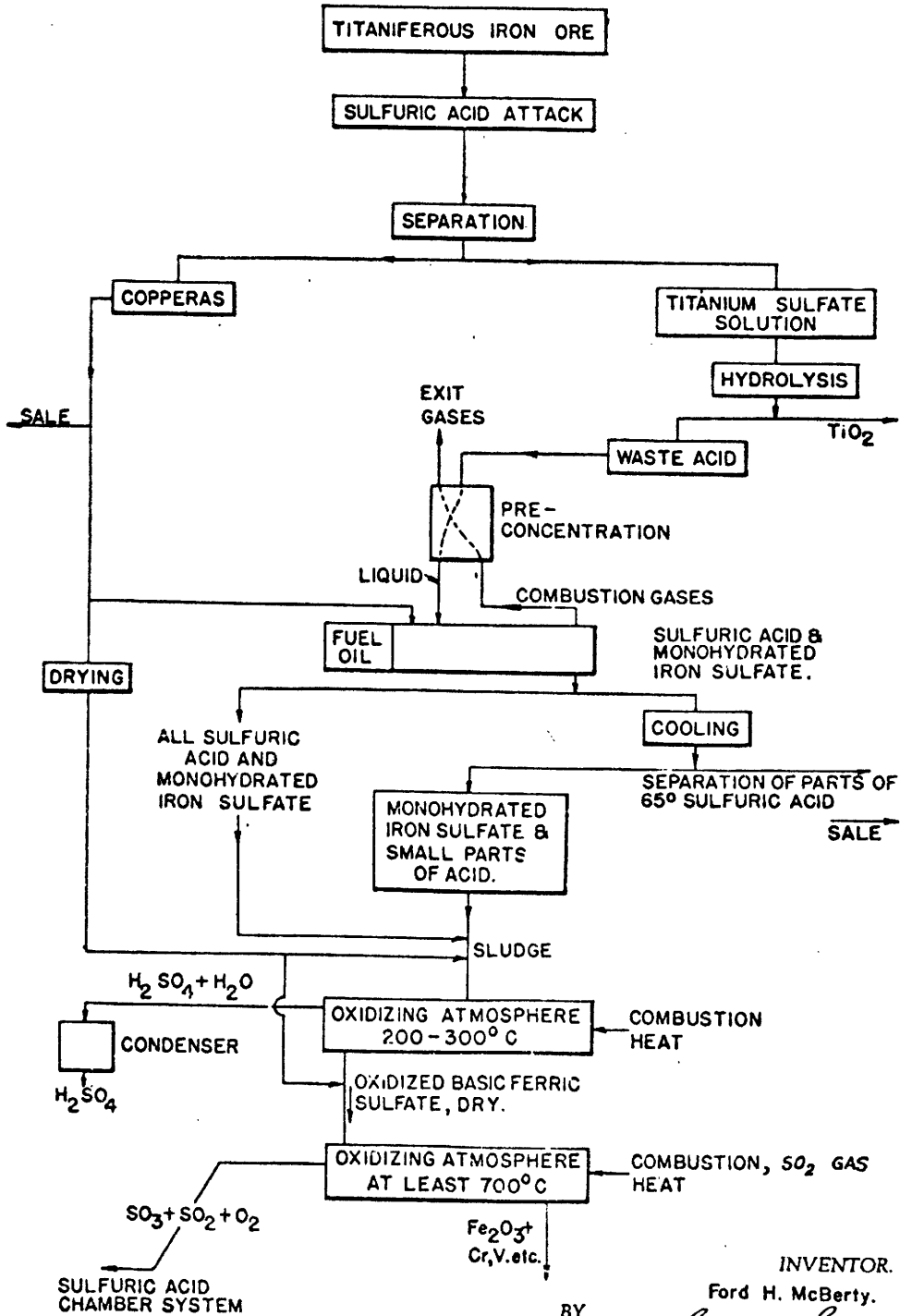
TREATMENT

SULFURIC ACID RECYCLING

Nov. 2, 1937.

F. H. McBERTY
UTILIZATION OF WASTE PRODUCTS IN THE MANUFACTURE
OF TITANIUM COMPOUNDS FROM TITANIUM ORES
Filed Feb. 15, 1936

2,098,056



INVENTOR.

Ford H. McBerty.

BY *[Signature]*
ATTORNEY.

AUSGABETAG: 10. MAI 1962

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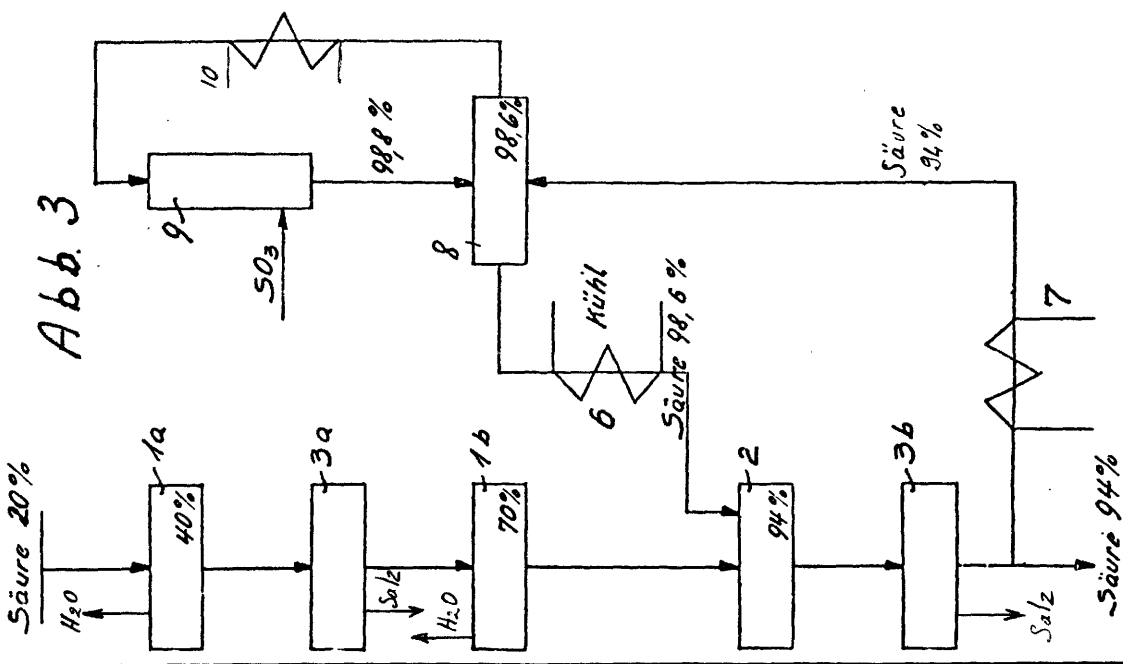
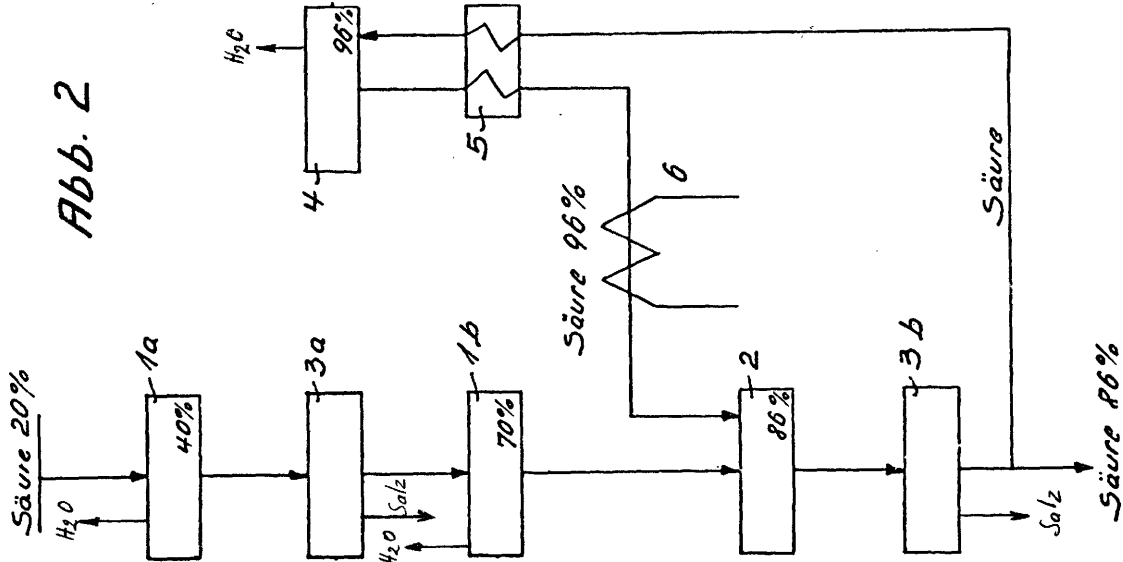
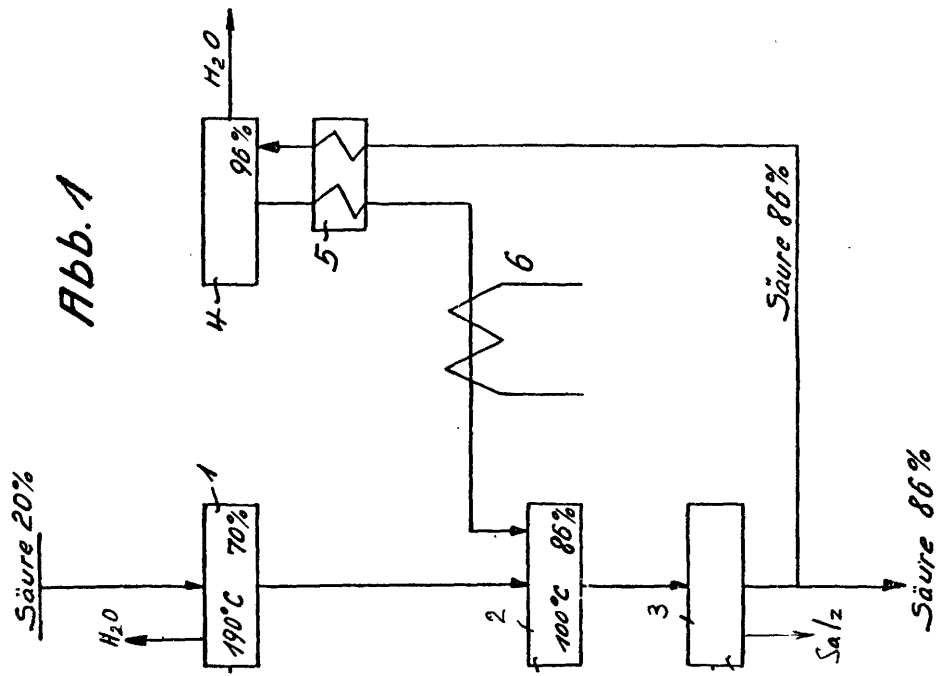


Abb. 3

TREATMENT

CALCIUM SULFAT DECOMPOSITION
LURGI PROCESS**Herstellung von Schwefelsäure
und Zement aus Gips****Verfahren Müller-Kühne**

Für die Erzeugung von Schwefelsäure können – außer Elementarschwefel, Pyrit und anderen sulfidischen Erzen – auch Gips bzw. Anhydrit oder Abfallgips aus chemischen Prozessen als Rohstoffe genutzt werden. Dabei wird neben Schwefelsäure auch Zement erzeugt. Die Lurgi Gesellschaft für Chemie und Hüttenwesen und die Polysius GmbH, Neubeckum, planen, konstruieren und liefern gemeinsam derartige Anlagen.

Ausgangsmaterial

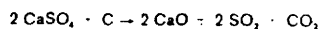
Gips bzw. Anhydrit oder
Abfallgips, z. B. aus der Phosphorsäureherstellung
Ton, Zuschlagstoffe, Reduktionskoks.

Erzeugnisse

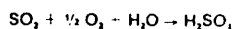
Schwefelsäure, Oleum
Portland-Zement

Verfahrensprinzip

Das Kalziumsulfat des Ausgangsmaterials wird mit Koks bei Gegenwart von Ton und Zuschlagstoffen in einem Drehrohrofen bei Temperaturen um 1400 °C gespalten:



Das entstandene Kalziumoxid bildet mit Ton und den Zuschlagstoffen Portlandzementklinker. Das SO_2 wird katalytisch zu Schwefelsäure umgesetzt:

**Arbeitsweise**

Der zerkleinerte und getrocknete Gips wird – zusammen mit Ton, anderen Zuschlagstoffen und Koks in einer Mahltrocknungsanlage auf Rohmehlfineinheit aufgemahlen; Abfallgips wird zuvor getrocknet, kalzinert und dann getrennt zugemischt. Das Mischgut wird im Drehrohrofen gebrannt, der entstehende Zementklinker wird gekühlt und gelagert.

Der Klinker wird auf Mehlfineinheit gemahlen; der Zement wird in einem Silo gelagert und anschließend verpackt und verladen.

Das SO_2 -haltige Ofenabgas wird in einer Gasreinigungsanlage entstaubt, gekühlt und kontaktreif gereinigt.

Nach der Trocknung und Aufheizung der SO_2 -Gase in Wärmeaustauschern auf Reaktionstemperatur erfolgt die katalytische Umsetzung des SO_2 zu SO_3 in der Kontaktgruppe.

Das SO_3 wird in Form von Schwefelsäure oder Oleum absorbiert und die Säure zur Stapelanlage oder zum Verbraucher gefördert.

Technische Daten

Mindestgrößen der Anlagen: 200 bis 300 t/a Schwefelsäure bzw. Zement.

Ungefährer Betriebsmittelbedarf pro 1 t Zement + 1 t Schwefelsäure:

Kalziumsulfat (CaSO_4): ca. 1,6 t

Ton: ca. 0,3 t

Zuschlagstoffe: ca. 0,14 t

Reduktionskoks: ca. 0,13 t

Kühlwasser: ca. 50 m³

Elektrische Energie

für den Zementteil: ca. 130 kWh

für Gasreinigung und Schwefelsäureteil: ca. 50 kWh

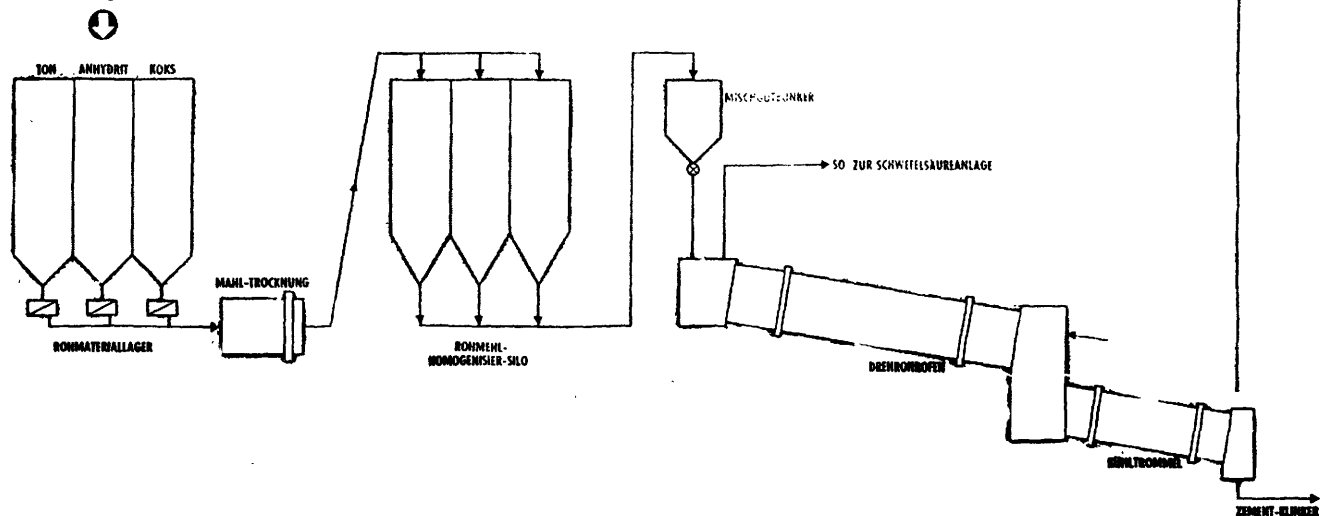
Wärmebedarf

für Klinkerbrennen: ca. 1,6 Mio. kcal;

für Trocknung und Kalzinierung des Rohgipses:

je nach Herkunft unterschiedlich, für Naturgips

z. B. 420.000 kcal



2,926,070

DECOMPOSITION OF AMMONIUM SULFATE

Thomas H. Milliken, Jr., Moylan, Pa., assignor to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

Application February 23, 1954, Serial No. 412,022

4 Claims. (Cl. 23-167)

This invention relates to the treatment of ammonium sulfate and ammonium hydrogen sulfate to recover therefrom ammonia and the oxides of sulfur. It is more particularly concerned with the method of operation and with the recovery of the oxides of sulfur and particularly of the sulfur trioxide.

The disposal of large amounts of sulfuric acid which have been partially spent in the course of various treatments is frequently a serious economic and/or waste disposal problem confronting industries employing sulfuric acid in their process or systems. This problem is particularly existent in such industrial operations where sulfuric acid in large volumes is employed, such as for example in the sulfuric acid treatment of various petroleum products and in the acid treatment of clays for the production of decolorizing materials and acid-activated cracking catalyst as for the petroleum industry. The amount of sulfuric acid employed frequently is of such large volume initially that the recovery thereof would be highly desirable for financial reasons. In such instances where the economic recovery has not been practical, the safe disposal of the spent acids has been a continuing problem of appreciable extent in that there is always the possibility of creating atmospheric or stream pollution situations.

This invention provides for the economic handling of these wastes in suitable manner such that the materials may be reused and the waste disposal problem reduced to a minimum. It also provides a method whereby sulfuric acid is neutralized with ammonia and the ammonium sulfate or ammonium acid sulfate thus produced is readily and economically converted to useful products including ammonia and the oxides of sulfur.

The neutralization of sulfuric acid wastes with ammonia is an operation of long standing and is widely practiced commercially, mainly for its value in reducing the waste disposal problem rather than for its economic desirability in the production of an advantageously marketable product in the ammonium sulfate. Much of the ammonium sulfate thus produced commercially is marketed as a fertilizer which is in competition with other sources of ammonium sulfate and other fertilizer materials and is not completely economic to any high degree of desirability.

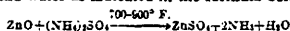
The present invention, however, has among its objects the provision of an economic method for the recovery of both ammonia and the oxides of sulfur from ammonium sulfate and ammonium acid sulfate. Another object is the recovery of these materials in a form suitable for their use, per se or with a slight additional treatment, again and again in the process, particularly as fresh sulfuric acid from the oxides of sulfur and as a neutralizing agent in the form of ammonia.

In accordance with this invention ammonium sulfate and/or ammonium acid sulfate is introduced into contact at converters to produce gaseous ammonia and metal sulfate with a bed of high surface area particulate contact mass comprising a metal oxide readily convertible to a sulfate and which sulfate decomposes at relatively moderate temperatures in the range of 1100-1800° F. to the metal oxide and gaseous oxides of sulfur. The gaseous ammonia from the decomposition of the ammonium sulfate is separated from the bed and separately recovered, and the bed containing the metal as the sulfate is heated to a temperature sufficiently high to decompose the metal sulfate to the oxides of sulfur and metal oxide. The thus produced oxides of sulfur, namely sulfur dioxide and sulfur trioxide, are separated from the bed containing the metal oxide and the sulfur trioxide is used for concentrating somewhat diluted sulfuric acid for further use.

A better understanding of this invention will be obtained by referring to the attached drawing and to the description and claims which follow.

In the drawing the single figure is a diagrammatic exposition of one embodiment of the invention.

The primary concern for the successful operation of this process is the contact agent to be employed. Metal oxides of the type coming within the description and bounds of this invention, that is, capable of forming heat decomposable sulfates which revert to the oxide with concomitant evolution of the oxides of sulfur, are relatively widely known and include iron oxide in some of its forms, cerium oxide, chromium oxide, zinc oxide and many others. These oxides, of which zinc oxide is a preferred embodiment, react with ammonium sulfate at moderate to high temperatures in the range of about 500° to 1000° F. and preferably about 700° to 900° F. to form with the evolution of heat the metal sulfate, ammonia and water as indicated in the formula below:



This type of reaction is utilized in the operation of the

present process with, however, the success thereof depending on the maintenance of high surface area available at all times in the convertible metal, as in either oxide or sulfate form but particularly in the oxide form. For instance, zinc oxide may be prepared with relatively high surface area which, beyond relatively few cycles from the oxide to the sulfate, loses its essential characteristic of high surface area with the result that while the zinc oxide is still chemically capable of performing the desired reaction, the surface area has been reduced to such a low level that the surface of the oxide available to the reaction is so limited the rate of reaction is reduced to an impractically low degree. This condition of reversion to a massive or bulky form of low surface area is not limited to zinc oxide, but is a condition which is arrived at either sooner or later with any of the other possible convertible oxides. The success of the present process, therefore, depends on the preparation of a contact agent comprising these convertible oxides which have not only initially the desired high surface area (in the order of 20-200 square meters per gram) but will continue to have a practical high surface area throughout the operation of the process so that their successful participation in the reaction will be retained at a practically high level for any period of time.

It has been found that the convertible metal oxides of the required attributes are unsuccessful for use by themselves regardless of the extent of their surface area as initially prepared in that the heats of formation and changes in the chemical state result in changes in the crystal structure which lead to the loss of surface area through the inherent increase in crystal size. This is overcome in accordance with my application Serial No. 29,176, filed November 10, 1952, now abandoned, of which my present application is a continuation-in-part, by depositing a suitable quantity of a convertible metal oxide on a high surface area support relatively inert to the conditions of the reactions encountered in this system.

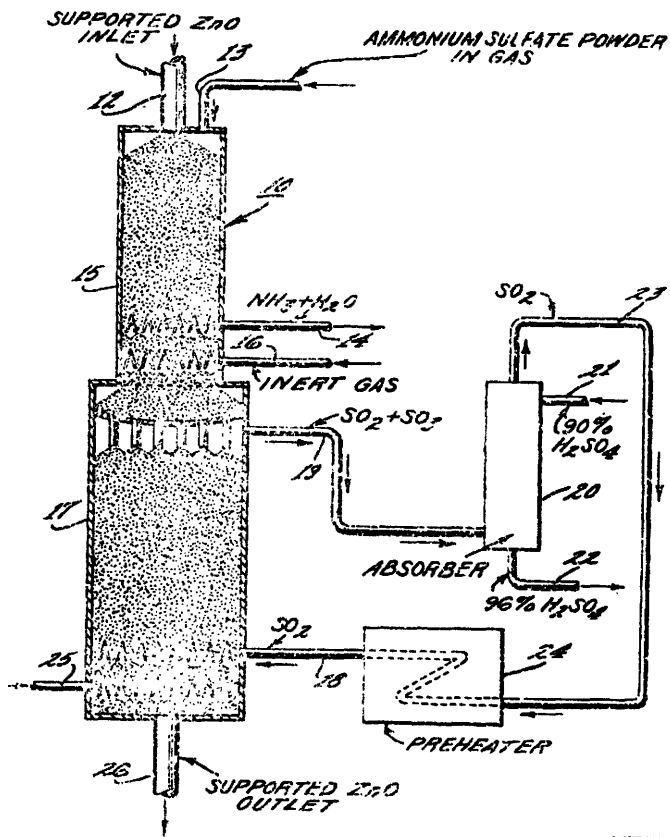
Feb. 23, 1960

T. H. MILLIKEN, JR

2,926,070

DECOMPOSITION OF AMMONIUM SULFATE

Filed Feb. 23, 1954



INVENTOR.
 Thomas H. Milliken, Jr.
 BY *W. H. Wood*
 ATTORNEY

TREATMENT

METAL CHLORIDE HYDROLYSIS
WOODALL DUCKHAM PROCESS

Chloride liquor is pumped to the preconcentrator, which is a simple packed tower. In this the hot roaster gases are desuperheated by contact with the feed liquor. This evaporates up to 25% of the water in the feed, thus maintaining maximum heat efficiency. The concentrated liquor is pumped to the roaster, where it is sprayed through atomisers near the top. As the droplets fall, they are first evaporated to dryness in the upper zone, and then decomposed in the lower high temperature zone. Heat is provided by combustion products introduced tangentially near the reactor base. The product oxide falls to the base of the reactor where it is discharged usually as cenospheres (hollow spheres), typical of spray dried materials. The cenospheres are loosely agglomerated fine particles in the sub-micron range, and this gives the material its high surface area and activity.

The gases leaving the reactor top contain combustion products, water vapour and HCl. These gases pass through cyclones for entrained solids removal, through the preconcentrator for heat recovery, and then to the absorber. This is normally a simple adiabatic packed tower producing acid of 18 - 20% HCl. In certain cases it is possible to use cooled absorbers to recover acids up to 36% HCl. In the adiabatic system water for absorption can be weakly acidic rinse waters from other processing stages, thus eliminating further effluent problems. After absorption, the waste gases are exhausted to atmosphere, thus maintaining the plant under slight negative pressure.

Because the decomposition process is carried out truly counter-current, it is normally only necessary to operate at temperatures of 600-750°C in the reaction zone, and 300-400°C at the outlet.

This permits the use of very simple mild steel/alumino-silicate refractory construction without risk of corrosion or erosion.

Combustion products are generated in simple burners of conventional design, burning any of the commercial liquid and gaseous fuels.

Because of its basic simplicity, the process is very stable, very flexible and capable of processing liquors of widely differing compositions from water to saturated solutions. Labour and maintenance requirements are kept to a minimum.

Typical operating data

- For a plant processing 4,500 litres per hour of feed liquor containing 20% FeCl₂ and 5% HCl (typical spent leach liquor)
- Heat Input 3.3 x 10⁶ K.Cal/hr
- Power 170 Kw
- Process Water 700 litres/hr
- Absorber Water 4,000 litres/hour (This may be spent wash waters)
- Labour 1 Man/shift
- Regenerated Acid 18% HCl: 4,500 litres per hour

Pilot Plant

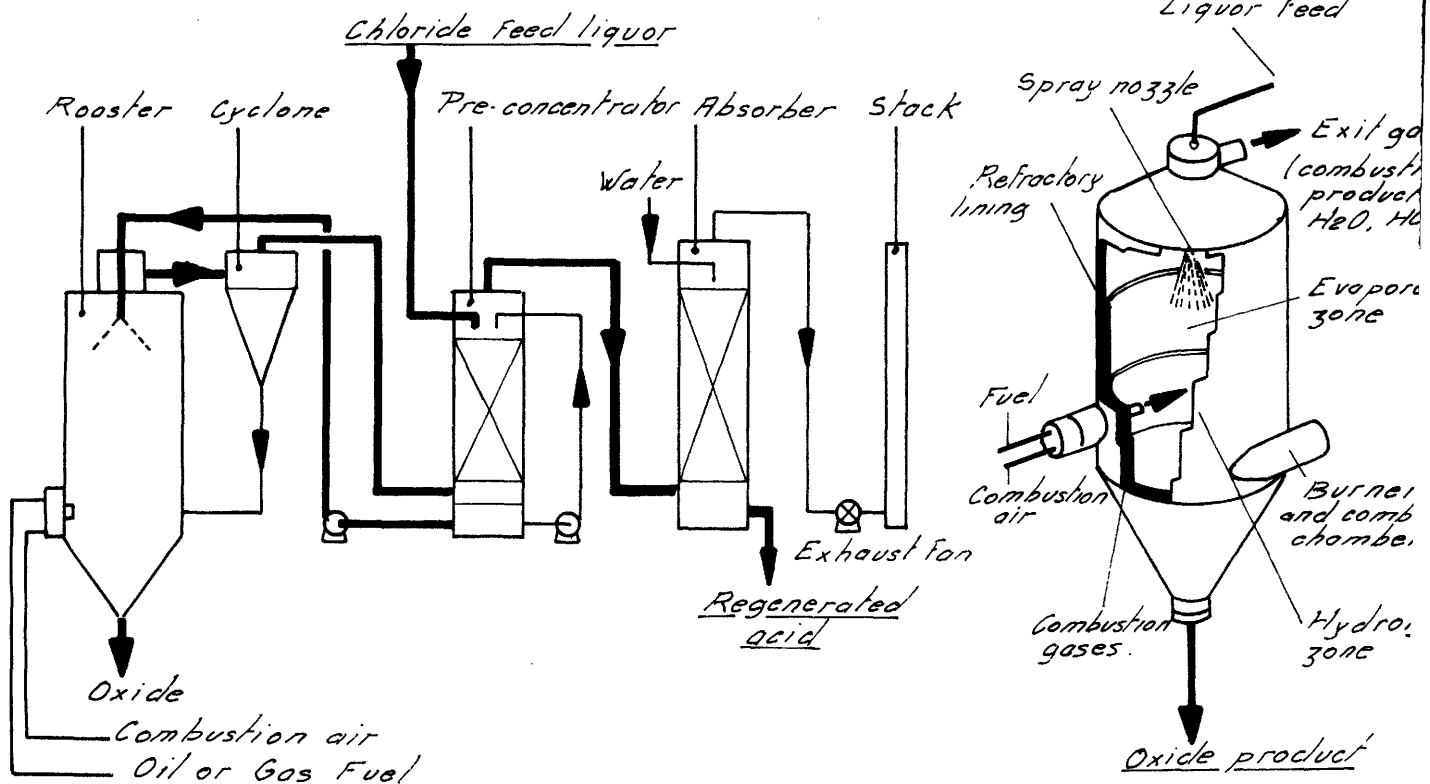
Full pilot plant facilities are available at our Experimental Station at Heywood, Lancashire, where client's liquors can be processed, and where complete mineral and metallurgical treatment processes can be developed.

Worldwide Activities

The worldwide success of the process has been greatly assisted by our fully integrated design and construction facilities in Australia and South Africa and by engineering agreements covering Europe, North America and Japan.

W.D Spray Roasting Process

Spray Roaster



TREATMENT

METAL CHLORIDES HYDROLYSIS

LURGI PROCESS

(Taken from Lurgi Handbook)

15.4 Beizbad-Regenerierung

System Lurgi

(LW)

Beim Beizen von Bändern, Blechen, Rohren, Draht, Profilen, usw. wird der noch anhaftende Zunder mit wäßrigen anorganischen Säuren gelöst. Neben dem bisher vorherrschenden Beizen mit Schwefelsäure gewinnt in neuerer Zeit das Beizen mit Salzsäure stark an Bedeutung.

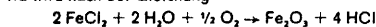
Der Zunder löst sich als Eisen-II-sulfat bzw. als Eisen-II-chlorid im Beizbad, dessen Säurekonzentration sich gleichzeitig um äquivalente Beträge vermindert. Bei chargenweisem Betrieb würde sich das Beizbad relativ schnell erschöpfen, zudem würden erhebliche Substanzverluste und Abwasserprobleme entstehen. Man regeneriert daher kontinuierlich: Aus dem Beizbad wird laufend ein der Eisenaufnahme entsprechender Teilstrom entnommen; nach Entfernung der gelösten Ei-

sen-III-oxid wird er – mit Säure aufgestärkt – dem Beizbad wieder zurückgegeben. Das Beizbad kann dadurch ständig auf der gewünschten Säure- und Eisenkonzentration gehalten werden.

Das technische Problem ist die Entfernung der Eisensalze aus den Beizbädern. Beizbad-Regenerieranlagen nach dem System Lurgi entfernen das Eisen aus schwefelsäurehaltigen Bädern durch Vakuum-Kristallisation (15.3) in Form von Eisen-II-sulfat-Heptahydrat, aus salzsäurehaltigen Bädern das gebildete Eisen-II-chlorid durch hydrolytische Spaltung und Oxidation zu Eisen-III-oxid unter totaler Rückgewinnung der Salzsäure.

Das zu regenerierende Beizbad wird bei gleichzeitiger Wasserverdampfung unter Vakuum auf Temperaturen zwischen 5 und 0°C gekühlt. In diesem Temperaturbereich kristallisiert das Eisensulfat als Heptahydrat ($\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$); es wird abzentrifugiert und kann z. B. thermisch in Eisenoxid und Schwefeldioxid gespalten werden. Die Mutterlauge fließt in das Beizbad zurück, das mit Schwefelsäure und Wasser aufgerichtet wird.

Regenerierung salzsaurer Beizbäder: Das im erschöpften Beizbad enthaltene Eisen-II-chlorid wird nach der Gleichung



in Eisen-III-oxid und freie Salzsäure gespalten. Das Eisenoxid wird von den Spaltgasen getrennt, die in den Spaltgasen enthaltene Salzsäure geht in den Beizprozeß zurück.

Bad aufgelöst und in den Reaktor zurückgeführt. Die im Vorverdampfer abgekühlten Gase strömen mit den dort anfallenden chlorwasserstoffhaltigen Brüden in den adiabatisch arbeitenden HCl-Absorber.

Für die HCl-Absorption wird Beizbad aus der Beizanlage entnommen und in den Absorber gefördert. Dabei stärkt sich das Beizbad um 2 bis 3% HCl auf. Die gesamte in den Regenerationsprozeß eingeführte (freie und gebundene) Salzsäure wird dadurch zurückgewonnen, der Säurekreislauf ist somit geschlossen.

Absorbiert man den Chlorwasserstoff in Wasser, gegebenenfalls in Wasser aus der Spülung, so kann reine Salzsäure bis zu 20% HCl gewonnen werden.

Die aus dem Absorber austretenden Brüden werden in einem Kondensator niedergeschlagen, die nichtkondensierbaren Gase gehen über einen Ventilator ins Freie.

Die Eisenoxidproduktion wird aus dem Wirbelbett abgezogen.

Technische Daten

Regenerierung schwefelsaurer Beizbäder:

Obliche Auslegung: für Beizanlagen mit Leistungen ab 1000 t/mo Stahl bis zu höchsten Durchsätzen

Korngrößen des Heptahydrates: ca. 0,4 mm

Feuchtigkeit des Heptahydrates: unter 0,3%

Regenerierung salzsaurer Beizbäder:

Leistungen: ab 100 l/h verbrauchtes Beizbad bis zu beliebig hohen Durchsätzen

HCl-Rückgewinnung: vollständig

Anfallendes körniges Eisenoxid:

Schüttgewicht: 2,5 kg/l

Chlorgehalt: unter 0,05 %

Arbeitsweise

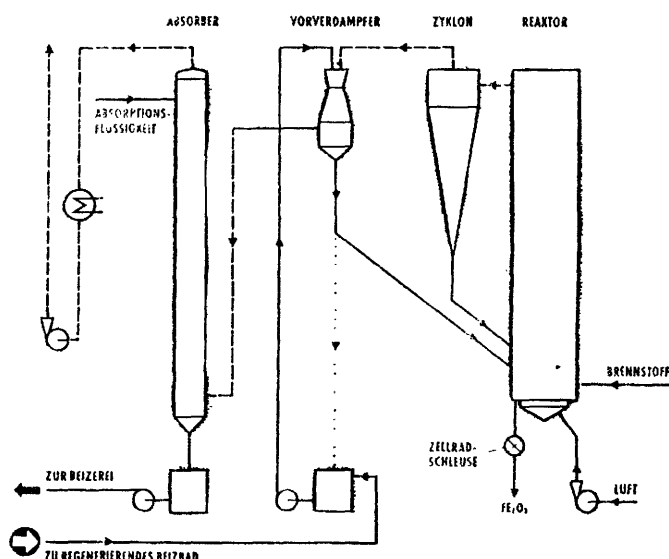
Regenerierung schwefelsaurer Beizbäder:

Die Arbeitsweise der Regenerierung schwefelsaurer Beizbäder entspricht weitgehend der unter 15.3 beschriebenen Arbeitsweise der Kristallisation durch Verdampfungskühlung. Söll aus wirtschaftlichen Gründen (Transportkosten!) Monohydrat statt Heptahydrat erzeugt werden, so wird ein Zerstäubungstrockner (15.5) zur Entwässerung des Heptahydrates nachgeschaltet.

Regenerierung salzsaurer Beizbäder (vgl. Apparatschema):

Eine dem Eisenverlust im Beizprozeß entsprechende Menge verbrauchtes Beizbad wird in den Vorverdampfer gefördert und dort mit den aus dem Reaktor kommenden heißen Gasen in direktem Wärmeaustausch weitgehend konzentriert. Die konzentrierte Säure fließt unter Eigendruck in den Reaktor, wo in einem mit Luft aufgewirbelten Bett von Eisenoxid-Körnern bei Temperaturen von etwa 800 °C die restliche Verdampfung und die Zersetzung des Eisenchlorids in Chlorwasserstoffgas und Eisenoxid stattfinden. Der Reaktor kann mit Öl oder Gas beheizt werden.

Die heißen Röstgase, die den Reaktor am Kopf verlassen, enthalten Chlorwasserstoffgas, überhitzten Wasserdampf, die Verbrennungsprodukte der Heizmedien sowie kleine Mengen Eisenoxidstaub. Letzterer wird in einem Zyklon von den Röstgasen getrennt und in das Wirbelbett zurückgeführt. Im Vorverdampfer geben die Röstgase den größten Teil ihres Wärmeinhaltes zur Konzentrierung des zu regenerierenden Beizbades ab. Dabei werden auch die in den Röstgasen noch vorhandenen Eisenoxid-Teilchen in dem konzentrierten



TREATMENT

PICKLING LIQUOR REGENERATION
JAPAN SOLEX PROCESS

Taken From Chemical
Economy and
Engin Review

3. Recovery of HCl from Waste Hydrochloric Acid

So far the thermal-decomposition process has usually been used to regenerate hydrochloric acid used for pickling metallic materials or articles which contains abundant heavy metallic ions. By the above process, Fe_2O_3 and HCl are recovered by decomposing waste HCl sprayed into the furnace maintained at high temperature. However, there are some significant disadvantages such as severe corrosion of apparatus by Cl_2 gas evolved with a large amount of water, high maintenance cost and low rate of operation of apparatus. Further, when the concentrations of heavy metallic ions are low in waste acids, the extremely large consumption of energy is required for thermal-decomposition. Therefore, it becomes very important to control the concentration of metallic ions in waste acids.

Our process has overcome the disadvantages of the conventional process, is independent of the Fe concentration in waste acids and can regenerate spent acids by extraction and removal of Fe ions in waste acids as a dense solution of those.

Describing in a concrete form, oxidation-reduction cell is formed between an anode compartment of diaphragm-electrolysis into which waste acids are introduced and a cathode compartment into which a concentrated solution containing Fe-HCl complex back-extracted is fed. Consumption of electric energy is extremely reduced by transferring and recovering free HCl in the cathode compartment into the anode compartment with oxidation of Fe^{2+} ions in waste acid to Fe^{3+} ions. Thus, the oxidation-reduction process can be simplified and the consumption of electric energy in the following Fe electrolysis process can be reduced. The solution in which free HCl ions were transferred to the anode compartment and Fe ions were reduced to Fe ions are mixed into the recycling solution in the following electro-reduction compartment. Fe is recovered as an electrolytic iron, while Cl ions are recovered as HCl with transferring to the other compartment. It is possible to maintain the most suitable condition for electrolysis such as a capable addition of electrolyte since the recycling solution in the electro-reduction compartment is separated from an acid system.

Therefore, the energy cost required for electrolysis is not so

different from that of the conventional thermal-decomposition process and moreover the high-purity electrolytic iron can be obtained. When other ions such as Zn Pb ions except Fe ions present in waste acids and concentrations of these ions become high, the one part of solution after the extraction of Fe ions is fed to the extraction stage of Zn and Pb and then these ions can be extracted and recovered.

As described above, the present process has the following features.

- 1) The metallic ions included in waste pickling solution can be recovered as an additional valuable form by the extraction of them from it.
- 2) The electrolysis process can be separated from the acid lines and operated as an independent system.

It is very easy to select the corrosion-proof materials because all processes are operated at ordinary room temperature and to control the Fe ions in the pickling solution. In comparison with the conventional thermal-decomposition process, the maintenance cost and labor cost in this process can be further reduced due to less corrosion parts and easier operation control. If the recovered electrolytic iron is high-purity and is on the market as a powder, the market of several thousands tons per year in value of 100,000 yen/ton would be considered.

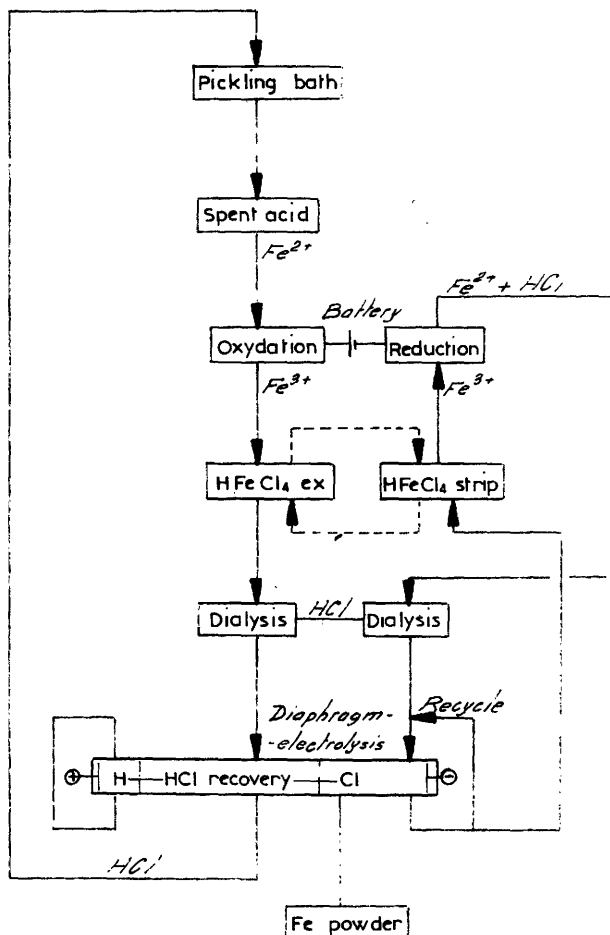


Table 2 The comparison of this process to the thermal-decomposition process

	Thermal-decomposition process		Sorex process	
	Capacity 1,000 kt/y Fe 90 g/l 83m ³ /d X 30 days	¥600,000,000	Capacity 1,000 kt/y Fe 60 g/l 125m ³ /d X 30 days	¥600,000,000
Running cost				
Fuel	188 kl/month	¥ 5,264,000	10 kl/month	¥ 280,000
Power	80 X 10 ³ kWh/month	¥ 640,000	1,125 X 10 ³ kWh	¥ 9,000,000
Solvent loss			0.8t/month	¥ 1,200,000
35% HCl loss	80t/month	¥ 1,520,000	3t/month	¥ 57,000
Insurance		¥ 15,000,000		¥ 15,000,000
Maintenance cost		¥ 5,000,000		¥ 2,000,000
Labor cost	(9 men)	¥ 3,750,000	(6 men)	¥ 2,500,000
(Total)		(¥ 31,174,000)		(¥ 30,037,000)
35% HCl	1.584t/month	¥ 30,096,000	1.661t/month	¥ 31,559,000
Fe ₂ O ₃ or Fe	313.7t/month	¥ 1,569,000	Fe metal 225t/month	¥ 11,250,000
(Total)		(¥ 31,665,000)		(¥ 42,809,000)
Balance	¥491,000/month		¥12,772,000/month	

Chlorine made in the modern style without caustic

Kellogg's improved version of the old Deacon process for converting hydrogen chloride into chlorine will get commercial trial in Du Pont's fluorochlorohydrocarbons plant

Almost 100 years after it was introduced in Europe, the Deacon process for making chlorine from hydrogen chloride will get its first crack at the big-time in the U.S. A modified version, called the Kel-Chlor process by developer M.W. Kellogg, will be installed to recover 600 tons/day of chlorine from by-product HCl at a fluorochlorohydrocarbons plant planned by Du Pont for Corpus Christi, Tex. (*CW Technology Newsletter*, Apr. 12).

The plant—the biggest in the world when completed—will be installed in stages. The first stage, a complex to produce chlorohydrocarbons, will be able to turn out 500 million lbs./year of carbon tetrachloride, perchloroethylene and chloroform, the starting materials for Du Pont's line of fluorocarbons, tradenamed Freon. This unit is scheduled to start up by late '73. The Freon plant, next to be completed, will have approximately the same capacity.

Du Pont says the big scale of the plant and the advanced technology to be employed will cut production costs. The company will not elaborate on that, but it's easy to see how Kel-Chlor ties in nicely. Making carbon tet by chlorinating a hydrocarbon, for instance, is a substitution chlorination; half the chlorine introduced ends up as hydrogen chloride. Then, in making dichlorodifluoromethane (Freon-12), hydrogen fluoride reacts with the carbon tet, generating two more mols of hydrogen chloride. The net reaction involves use of eight chlorine atoms, six of which end up in the form of by-product hydrogen chloride.

The new plant itself also would appear to fit well into Du Pont's over-all operating scheme. For instance, the company will probably bring in hydrogen fluoride from the unit it is building in a joint venture with Mexican companies (*CW*, Aug. 4, '71, p. 12). Du Pont has been a big buyer of carbon tet. But it has generated an extremely pure grade of HCl from hydrofluorination. This HCl has been used

in the manufacture of neoprene and alkyl chlorides.

Du Pont says it has no plans to change its present Freon manufacturing operations while the Corpus Christi plant is being built. But it seems likely that when the plant begins operating at least some of the older capacity will be shut down. In the meantime, Du Pont's needs for by-product are declining, since it is phasing out its acetylene-based neoprene production in favor of the butadiene-based route. In fact, the butadiene process generates its own HCl by-product.

Improved Technology: The idea of recovering chlorine from by-product HCl has intrigued chemical companies for many years because it provides a way of reusing a waste product and, at the same time, getting chlorine at a price that is cheaper than on the open market.

Kellogg has piloted its process for three years in a scale-down of the design for the large Du Pont plant. The pilot unit "has proved the practicality of building a high-capacity Kel-Chlor plant having a high onstream factor," says John Dwyer,

ably, they would also produce chlorine at somewhat less than the open market price of about \$75/ton. But another factor in economic evaluation would be the merit of the method in recovering a waste product that would have to be disposed of, perhaps even treated before disposal.

For example, Kellogg sees Kel-Chlor's potential use as a part of processes that have been uneconomic because too much hydrogen chloride is produced along with the wanted material. "Any system that generates large quantities of hydrogen chloride could use Kel-Chlor," says Dwyer. Small quantities of hydrochloric acid, he claims, also could be converted in the same unit at little or no extra cost, "adding an antipollution aspect to the process by solving a disposal problem without increased power requirements."

Early Importance: The original Deacon process was an important source of chlorine in Europe for many years, particularly for bleaching powder for textile manufacture. But use of the method was discontinued after World War I, when chlorine consumption began to increase rapidly. It could not compete with electrolysis of brine because the chlorine content of the gas was low and purification was costly.

The process is a vapor-phase oxidation of HCl over a hot catalyst of manganese or copper salt (e.g., copper chloride) on an inert, porous carrier, such as pumice, at 430-475 C. Since air is used to furnish the oxygen, the chlorine product is highly diluted with nitrogen. And because the reaction is readily reversible, conversions are low (e.g., at 450 C, chlorine is 16% by volume, and HCl conversion is 66%).

Kellogg gets around the Deacon route's equilibrium limitations by using a more active catalyst (i.e., a combination of oxides of nitrogen—NO, NO₂ and NOCl) and adding sulfuric acid to soak up the water that forms. This shifts the equilibrium to the right, increasing the conversion into chlorine.

Not the First: Kellogg is far from the first to have attempted a Deacon im-

provement. I.G. Farben had a 10-tons/day pilot plant in operation during World War II, using the Oppau-Deacon process. And in '52, Hercules used a variation of the Oppau catalyst in a plant at Brunswick, Ga., that was designed to recover about 35 tons/day of chlorine from by-product HCl from the company's toxaphene plant. But problems with corrosion and a catalyst system forced shutdown of the unit within a few years.

Technical Enterprises (New York) worked up two processes in '57 that were piloted by Arco, Inc. But there have never been commercial installations.

Shell investigated a route to make chlorine by the air oxidation of nitrosyl chloride (Belgian patent 599,241). The company has never exploited the technique, says it has no plans to do so.

Allied also tried that approach, reacting salt (sodium chloride) with nitric acid to form nitrosyl chloride, which was oxidized to produce chlorine. The company operated a small plant, which has been closed for many years.

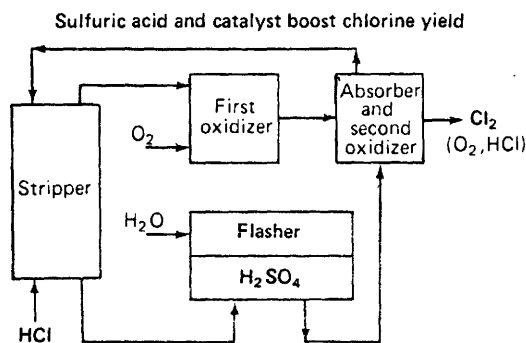
And Southwest Potash tried a variation on the same theme, using potash (potassium chloride) as the starting material. For several years it operated a plant in Vicksburg, Miss., reacting potash with weak nitric to make potassium nitrate and nitrosyl chloride. The chloride was then oxidized to yield chlorine by-product (*CW*, July 24, '65, p. 35).

Chlorine can also be made from hydrochloric acid by electrolysis. Processes are offered by Oronzio de Nora (Milan) and West Germany's Hoechst-Uhde, although only the plants built by Hoechst-Uhde are now operating. Also in Germany, Farbwerke Hoechst, runs a plant at Frankfurt, and Farbenfabriken Bayer has units at Leverkusen and Dormagen.

Bayer-Shell Isocyanates is starting up a plant in Antwerp, Belgium, and a Kuhlmann subsidiary, Soc. Technique et d'Enterprise Chimiques, will have a unit in operation this fall in France.

De Nora finds it is more profitable to sell HCl than to convert it into chlorine. And Uhde says European companies seem to have more surplus HCl than U.S. companies have. In fact, Uhde has talked with several U.S. companies, but its only electrolysis unit now operating on HCl in the U.S. is Mobay's 214-tons/day plant at an unidentified site.

Du Pont's use of the Kel-Chlor process is certain to rekindle interest in chlorine recovery from by-product HCl. It is also a development that chlorine producers will watch closely because any strong trend toward chlorine recovery could have an adverse effect on their business.



vice-president of research and engineering. It also showed that potential corrosion problems have been solved, he adds.

From a cost standpoint, a high-capacity Kel-Chlor unit is critical. Kellogg says chlorine can be produced for less than \$20/ton, but this is based on a unit with a capacity in the neighborhood of the 600 tons/day that will be operated by Du Pont. Other versions of the Kel-Chlor process that would be economic on a smaller scale are being studied. Presum-

Kellogg discusses worldwide Kel-Chlor ventures on-a toll basis

PULLMAN Kellogg, co-developer with Du Pont of the Kel-Chlor process for conversion of by-product hydrogen chloride to chlorine, is considering construction of such facilities in the UK, other European countries and in the USA on the basis of tolling arrangements.

The idea is to collect hydrogen chloride streams, which individually are too small to justify a separate Kel-Chlor plant but collectively make such a facility viable, and convert them to chlorine. This product is then returned to the respective hydrogen chloride suppliers.

The advantages of this concept were pointed out by Louis E. Bostwick, process development manager of Pullman Kellogg speaking at a Chlorine Institute

meeting in New Orleans last week. They include the "low fees for the conversion service due to economies of size; relief from the necessity for large capital expenditures; and an assured long-term means of disposal of by-product hydrogen chloride."

Apart from attracting interest in Europe and in the north-eastern and Gulf Coast states of the USA, Kel-Chlor plants are also being contemplated in the far east and preliminary discussions are underway with clients.

Kellogg is primarily looking for joint venture undertakings but has not decided on any definite ownership or operational details. It did add, however, that financing is "not considered to be a major problem in bringing the toll plant concept into reality."

Taken from E C N February 18, 1977

At present there is only one Kel-Chlor plant in operation; the 600 short ton/day facility at Du Pont's Corpus Christi complex in Texas which started up in 1974. But smaller units are feasible.

According to Kellogg for a one or two client toll facility (essentially over-the-fence) where use of the client's storage, or steam or other outside battery limits units, a plant with a capacity of 200-250 short ton/day is viable.

Energy requirements on these facilities are claimed to be a small fraction of other processes for conversion of hydrogen chloride to chlorine. The Du Pont unit was designed for more than 99 per cent overall conversion with no recycle from chlorine liquefaction.

However, Bostwick added that capital investment and operating costs can be lowered substantially if unconverted hydrogen chloride and oxygen are recycled. This allows use of less expensive materials of construction.

Bostwick also felt that integration of a Kel-Chlor plant with three particular chemical complexes—vinyl chloride, isocyanates and titanium dioxide—was especially advantageous.

CHLORINE REGENERATION TREATMENT KELLOGG PROCESS

Sizes from 20 to more than 600 ton/day and costs ranging from \$22 to \$55 per ton of chlorine, the Kel-Chlor process offers exceptional opportunities in chlorination chemistry

W. C. Schreiner, A. E. Cover, W. D. Hunter, C. P. van Dijk and H. S. Jongenburger,
The M. W. Kellogg Co., Houston

THE FIRST COMMERCIAL Kel-Chlor plant is onstream at E.I. du Pont de Nemours & Co., Inc's Corpus Christi, Texas, fluorocarbons complex. This 600-ton/day plant marks a decade of development first begun at the Kellogg Research Center and completed with Du Pont at one of its facilities.

The Kel-Chlor process converts hydrogen chloride (HCl) to chlorine by oxidation with oxygen through a chemistry route involving nitrogen oxide compounds and

a circulating sulfuric acid system.^{1,2,3,4} The process⁴ is not limited to a single set of design operating conditions, i.e., pressure, temperature, acid circulation rate and nitrogen oxides concentration. Higher pressures (to 15 ata) minimize reactor volumes but raise operating temperatures in critical areas which then require more corrosion-resistant materials of construction. The large Du Pont plant was designed for 15 atm and used tantalum cladding extensively. Smaller plants justify changes in conditions which permit brick lining, glass or Teflon.

Since current demand for HCl conversion plants is greatest in the 300 ton/day and smaller range, Kellogg has performed extensive redesign studies to offer a more suitable design—the low pressure Kel-Chlor I design. Further modifications are in pilot plant which will reduce investment costs and handle aqueous HCl feeds—Kel-Chlor II. With all these design versions, it is now possible to match almost any existing HCl conversion case. In addition, new possibilities are opened for large scale chlorine production.

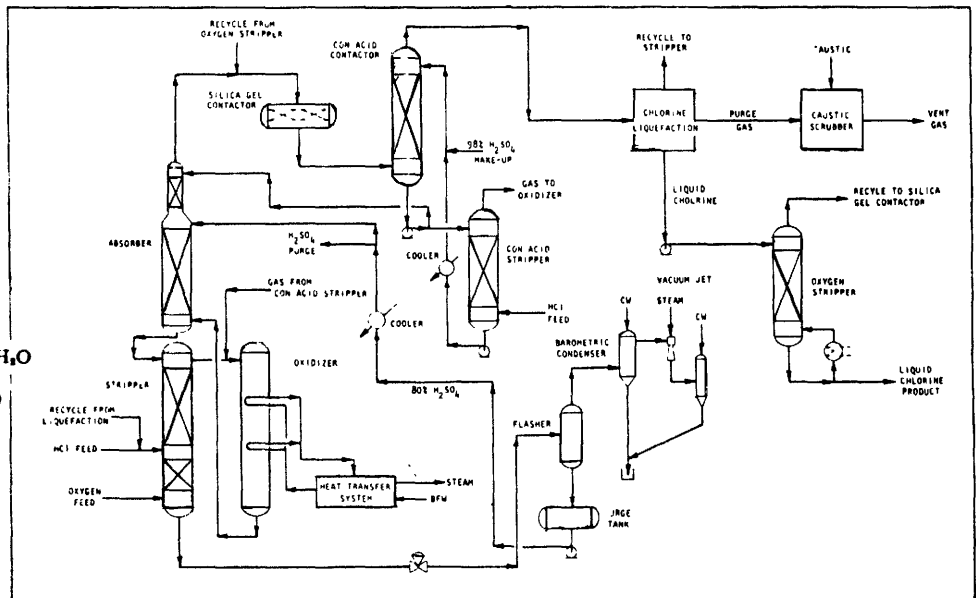
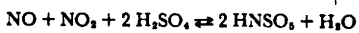
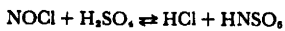
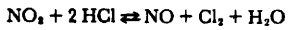
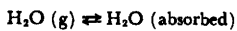
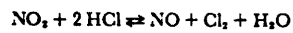
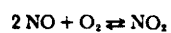
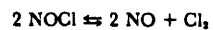
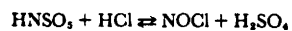
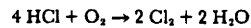


Fig. 2—Detailed schematic for Kel-Chlor I process.

TABLE 4—Chlorine manufacturing cost via the low pressure Kel-Chlor I process (90% Stream factor)

Fixed-capital investment* Materials	Units/ton Cl ₂	Unit cost	\$/ton Cl ₂	Plant size	
				300 ton/day \$7,900,000	75 ton/day \$3,450,000
HCl (100%)	1.034 ton	0	0		
Oxygen (99.5%)	0.231 ton	\$15/ton	3.47		
50% NaOH	6 lb.	\$0.04/lb.	0.24		
98% H ₂ SO ₄	28.6 lb.	\$0.015/lb.	0.43		
80% H ₂ SO ₄ production	29.8 lb.	\$0.01/lb.	(0.30)		
				3.84	3.94
Utilities					
Power	52.9 kwh	\$0.01/kwh	0.53		
Cooling water	9260 gal.	\$0.02/1000 gal.	0.19		
Boiler feed water	20 gal.	\$0.20/1000 gal.	0.01		
Process water	13 gal.	\$0.05/1000 gal.	0.01		
				0.74	0.74
Operating labor 2 men/shift @ \$5.00/man-hr.				0.89	3.53
Maintenance labor @ 2% of investment/yr.				1.60	2.80
General overhead @ 100% of labor.				2.49	6.33
Maintenance materials @ 3% of investment/yr.				2.40	4.20
Taxes & insurance @ 3% of investment/yr.				2.40	4.20
Depreciation @ 10% of investment/yr.				8.02	14.00
Total manufacturing cost				22.38	39.70

* The investment is based on U.S. Gulf Coast plant location and price estimated April 1974.

ANNEX 8-1

SYNTHETIC RUTILE SOLUBLE IN SULFURIC ACID
MURPHYORES PROCESS

Sulphuric Acid Solubility

While the main emphasis is on producing a rutile substitute for the manufacture of chloride pigment, titanium metal, and welding electrodes, the possibility of synthetic rutile substituting for ilmenite or high titania slags in the sulphate pigment industry under certain circumstances is not ruled out. The major technical consideration would be the solubility of the product in sulphuric acid. It is well known that mineral rutile is not soluble in sulphuric acid. However, murutile when produced under selected conditions of temperature of oxidation, reduction and calcination is sulphuric acid soluble. Our tests show that murutile analysing 91.5% TiO₂ as dried sample at 110°C (95.4% TiO₂ as calcined at 800°C), has a solubility of 97.5% of its TiO₂ content in 70% H₂SO₄ at its boiling point.

The results of x-ray studies (Figure 1) show that at all stages of leaching of "synthetic ilmenite" in the Murso process, the crystal form of titanium dioxide in the leached product (with and without calcination) is rutile. Thus the question of the solubility of titanium minerals is not necessarily tied up with rutile structure as is often believed. The solubility of murutile (which has a rutile structure) appears to be the result of the large surface area, porosity and defect structure (sub-grain size and grain boundaries) which is carried over into the end product from "synthetic ilmenite", which is produced during oxidation and reduction steps of the process. It is this very defect structure which enhances the reactivity of "synthetic ilmenite" during leaching in the Murso process. The significance of this phenomenon has been discussed in an earlier paper (5).

taken from T.M.S paper select

H.N Sinha

ANNEXE

SYNTHETIC RUTILE SOLUBLE IN SULFURIC ACID
BENILITE-S PROCESS

--- the firm recently announced Benilite-S (*Chem. Eng.*, Jan. 5, p. 76), developed (though not yet commercialized) as a feedstock for TiO₂ manufacture by the sulfate process. The advantage over unprocessed ilmenite ore: Sulphuric acid consumption plunges from about 3½ tons per ton of pigment to only 0.7-1.0 tons, with a corresponding drop in waste-acid volume for disposal. Exploiting Benilite-S, Weng stresses, can substantially reduce the equipment size of new TiO₂ plants, bringing capital cost savings that could justify small local installations.

••• The firm hasn't yet revealed the process modifications needed to make Benilite-S, but does point out that a key aspect of the technology is avoiding changes in the crystal structure of the ilmenite that would make the ore insoluble in sulfuric acid. Patent-pending modifications in the reduction-leaching steps, also still under wraps, overcome leaching troubles experienced with fine particles in ilmenite, yielding a lighter-colored beneficiated product more suitable for making Hitox. - - -

Taken from Chem. Engineering (76)

ANNEX 8-2-1 SYNTHETIC RUTILE - Murphoyes process
(taken from Murphoyes advertising brochure)

INTRODUCTION

RUTILE is the preferred source for the production of titanium metal, titanium dioxide pigment produced by the chloride route and coating for welding electrodes. While the supplies of rutile obtained by mining mineral sand deposits were for many years sufficient to satisfy the immediate demands of industry, there has been an underlying feeling that the industry would be limited by mineable rutile reserves. Thus with great foresight, Murphoyes, a Company which has been associated with the rutile mining industry since 1940, sponsored research in 1964 at Australia's premier minerals research establishment, the Division of Mineral Chemistry, CSIRO, into methods of producing a rutile substitute.

RESEARCH AND DEVELOPMENT

FROM the very outset of the research programme, the aim was to produce a material so close to natural rutile in physical (particle size) and chemical (composition, reactivity) characteristics, that it can substitute rutile in all its present applications. Also that the process developed should incorporate established technology and materials, and take into account the environmental problems which are of great significance in the pigment industry and are to a great extent responsible for the upsurge in the use of the chloride process for pigment production.

As a source of titanium, low grade titanium ore ilmenite which is relatively cheap and the reserves of which are ubiquitous and very large, was chosen. Since ilmenite ores vary a great deal in composition both in their TiO₂ content and the associated impurities, a further aim of the research work was to develop a process which is capable of treating all ilmenites irrespective of their origin and quality (rock, alluvial, high chromium ilmenites, etc), thus ensuring that both the source and supplies of feed stock would not limit the life and utility of the process developed.

MURSO PROCESS

FROM the fundamental studies, a breakthrough in technology was made and all the above objectives have been achieved. We have named the process "MURSO" (Murphoyes - CSIRO) and the product "MURUTILE". The Murso process was the first to upgrade ilmenite to a product containing 95-96% TiO₂ and is also unique because it is the only process so far reported, which provides a method of converting the hitherto unsaleable chrome contaminated ilmenites into a rutile grade product.

PILOT PLANT TESTS

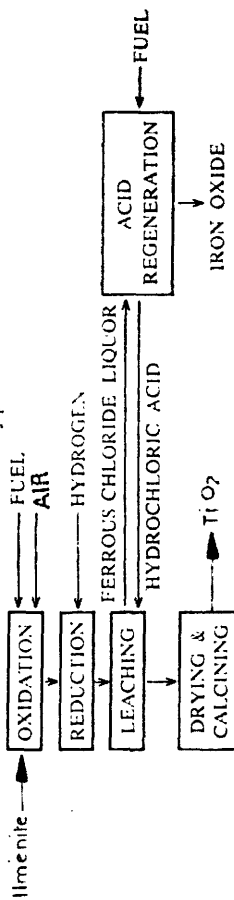
THE MURSO PROCESS which was tested extensively at the laboratory and bench scale at CSIRO using all commercially produced ilmenites, has been further refined and tested in a pilot plant. The pilot plant tests were a result of joint research and development agreement between Murphoyes and Mitsubishi Chemical Industries and were conducted over a period of two years at Mitsubishi Chemical Industries plant in Kurosaki, Japan. The engineering design data obtained from pilot plant tests have proven the technical and economic feasibility of the Murso process.

PATENTS

PATENTS covering the basic Murso process and improvements resulting from pilot plant tests and continued research activity have been granted in all major countries with ilmenite deposits and/or pigment plants.

PROCESS DESCRIPTION

THE MURSO PROCESS is elegantly simple and the principal steps of the process are set out in the primary flowsheet. The process has been described in detail in many publications.



LEACHING

LEACHING of reduced ilmenite is carried out continuously with hydrochloric acid (about 20% HCl) at atmospheric pressure and temperature of 105-110°C. During leaching iron and other soluble impurities (e.g. Mn, Mg, V, Al) contained in the ilmenite go into solution, leaving the leached mineral grain virtually unchanged in size from its original state. The ilmenite structure of the material, however, changes to rutile and the resulting synthetic rutile grain has a much larger surface area than a natural rutile grain and hence it chlorinates much faster and is also soluble in sulphuric acid.

DRYING and CALCINATION

THE leached material is filtered, dried and calcined to produce "Murutile". Depending upon the quality of the feed ilmenite, further physical processing e.g. magnetic separation to remove say chromite or other silicate minerals may be needed.

ACID REGENERATION

SINCE the ferrous chloride liquors from the leaching step are environmentally unacceptable for disposal and hydrochloric acid is usually too expensive to be used on a once through basis, an acid regeneration technique is employed. The method used involves high temperature hydrolysis of the ferrous chloride solution to give solid iron oxide and hydrochloric acid. The technology for this step is readily available on turn key basis now that many steel plants throughout the world are using hydrochloric acid for pickling and recycling HCl. The iron oxide produced is usually suitable for land fill but iron oxide for blast furnace feed can also be produced. Other options to treat the liquor for the recovery of valuable constituents e.g. vanadium, high grade iron powder or oxide, etc., are available as variations of the main process.

PRODUCT QUALITY

THE MURSO PROCESS has handled successfully in pilot plant and bench scale tests a very wide range of ilmenites. A typical result obtained is given in Table I.

TABLE I
Analysis of Ilmenite feed and Murutile

	ILMENITE FEED %	MURUTILE %
TiO ₂	54.6	95.5
FeO	23.7	—
Fe ₂ O ₃	1.3	1.3
MnO	1.7	0.05
Cr ₂ O ₃	0.04	0.02
ZrO ₂	0.41	0.63
Nb ₂ O ₅	0.08	0.15
V ₂ O ₅	0.38	0.06
MgO	0.32	0.01
Al ₂ O ₃	0.78	0.12
SiO ₂	0.52	1.0
Cl	—	0.06

CHLORINATION CHARACTERISTICS

SAMPLES of murutile have been tested for acceptability for use in chlorinators and murutile has met the specifications for particle size, cold and hot dusting, chlorine utilization and exothermicity value $\left(\frac{CO}{CO + CO_2}\right)$ during chlorination tests.

SULPHURIC ACID SOLUBILITY

MURUTILE is soluble in sulphuric acid and hence it can be used as feedstock in the sulphate process for making titanium dioxide pigment, thus solving the effluent disposal problems which have beset the sulphate process.

ENGINEERING DESIGN and KNOW-HOW

THE MURSO PROCESS described above is offered with numerous refinements which ensure that the technical efficiency of each stage is optimized and that environmental acceptability is maintained to very high standards. Also the engineering design concepts of the process have been fully developed and the innovations have been protected by patents as necessary. The know-how for a completely engineered plant can be offered on a world-wide basis.

SYNTHETIC RUTILE - ISHIHARA SANGYO KAISHA**Synthetic Rutile
(Rupaque®)**

"Rupaque" is the tradename for the synthetic rutile developed as a result of the Company's unique technology. In 1971, when competitors were still in the process

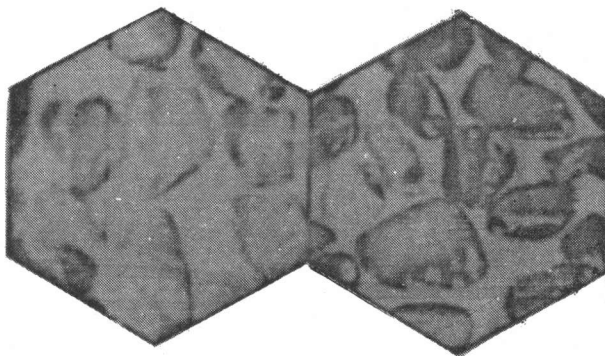
processed method is replacing the sulfate-processed production. The demand for titanium metal is also benefiting from a strong upward trend. These features have expanded the demand for natural and synthetic rutile to a greater degree year after year. While resources for natural rutile will inevitably deplete in the future, there are great expectations for synthetic rutile because of its stability of supply and quality. The Company received a number of orders for Rupaque in large quantities from leading overseas titanium dioxide, welding rod and titanium metal manufacturers and also received requests for increased deliveries from domestic titanium metal manufacturers. However, all orders could not be fulfilled due to the decline in production which was caused by the reinforcement of treatment facilities for pollution, including waste water and acid, regular repair and maintenance, and a series of accidents. However, as treatment facilities for pollution have been improved substantially and the reinforcement of the synthetic rutile plant has been completed, the facility is expected to be operating soon at full capacity.

During fiscal 1974, the Company sold 13,000 tons of synthetic rutile to domestic titanium metal manufacturers and 18,500 tons to chloride-processed titanium dioxide manufacturers in the United States, bringing the total sales output to 31,500 tons, representing an increase of 3,500 tons or 13% over the previous year.

The extremely tight supply-demand relations of natural and synthetic rutile have been reflected in prices of both types of rutile.

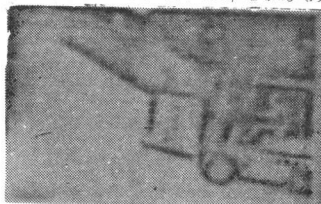
Since domestic sales and exports of the Company's Rupaque are in full swing and the price has strengthened considerably, Rupaque is an important contributor to the Company's profitability and is expected to play a substantial role in the future performance of the Company.

Taken from
Ishihara S.K.
Annual report 1974



of producing synthetic rutile on test plants, the Company was the first in the world to commence the manufacture of synthetic rutile of 2,500 tons per month on the commercial basis. The production capacity was reinforced several times and has reached 4,000 tons per month since April, 1974.

Synthetic rutile as a substitute for natural rutile is utilized in the manufacture of titanium dioxide by the chloride process, titanium metal, welding rods and other products in the same way as natural rutile. Making titanium dioxide through a chloride-



Taken from Ishihara S.K.
advertising brochure

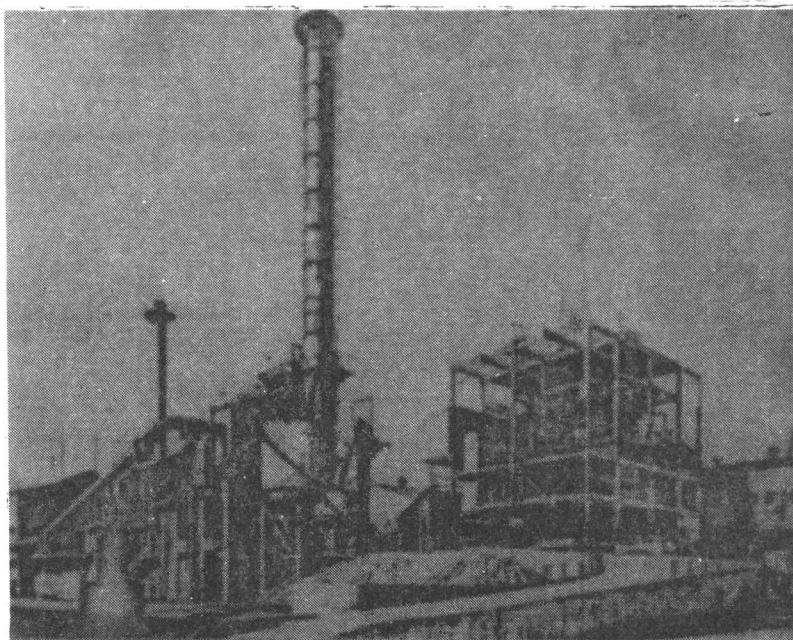
"Rupaque" Synthetic rutile

The consumption of natural rutile, the raw material for the manufacture of welding rod, titanium metal and chloride processed titanium dioxide, is increasing year after year. However, natural rutile is isolated only in Australia but for reasons of environment, its production has been ever decreasing, resulting in world wide shortage of supply.

In the circumstances, the emergence of a substitute for the natural rutile was strongly desired. Presently, in various countries of the world, many people are engaged in the research of synthetic rutile.

Our company, as the result of research for many years, successfully developed "synthetic rutile process" by dissolving iron and other impurities from partially reduced ilmenite utilizing the waste acid from titanium dioxide plant.

In 1971, forging ahead of other world-wide competitors, we constructed a 2,300 tons per month plant within the compound of our Yokkaichi Factory. Subsequently, the plant has been operating favourably, and presently, it has been expanded to a capacity of 4,000 tons per month. The product is sold to the manufacturers of chloride processed titanium dioxide, titanium metal, both domestic and foreign, under the brand name of "Rupaque", and it will be used as raw material to our own chloride processed titanium dioxide plant.



European Chemical News, February 18, 1977


Traditional attitudes change after recession**Japan sets new chemical priorities to overcome industry problems**

...In pollution control, another area of common concern, Japanese chemical firms are up against the strictest standards in the world, according to Takaoka. Taking just three examples: Japan demands almost total removal of nitrogen oxides from stack gases; the chloralkali industry is engaged in a total switch from mercury to diaphragm cells; and, according to one titanium dioxide producer, fully one-third of pigment production cost is accounted for by waste control.

Nevertheless, this could turn out to be a boon. If Europe and the USA eventually demand similar standards, Japan will have the advantage of operating in the same market but with partially or fully depreciated equipment.

The remaining two points are peculiar to Japan: high debt: equity ratios and the nature of employer-employee relationships. In the first case, because of their low equity base (typically 30 per cent) Japanese firms have to bear heavy fixed interest charges throughout a recession—in contrast to western firms, which can pass their dividends if necessary. . . .

...In the second, the "family-style" employment relationship enjoyed in Japan makes it practically impossible for firms to lay off workers during bad times. Added to this Japanese labour costs are already high: taking salaries and fringe benefits, workers are paid almost as much as in the US and more than in some European countries.

According to Takaoka, Japanese firms are making a five-fold response to these problems, seeking to increase profitability rather than their traditional goal of higher volume. Main strategies are: overseas investment, . . .

... Many companies are also making a virtue out of necessity and building new businesses on the back of the strict pollution requirements. Examples here are the Asahi Chemical, Asahi Glass, Maruzen Oil independently developed ion exchange processes for chlorine production and the Mitsubishi Gas Chemical process to produce terephthalic acid from toluene. . . .

Titanium Dioxide Business Shrinking

Titanium dioxide producers are planning to reduce titanium dioxide business, and to step up production curtailment of ammonium sulfate.

They have suffered from poor production economics due to increased expenditures for pollution control, slow recovery of domestic demand, and inflow of imported products.

The ammonium sulfate venture has shown the heaviest deficit.

Ishihara Sangyo Kaisha, Ltd., a leading titanium dioxide manufacturer, is making all-out efforts to extend its pesticide sector and to develop new chemicals.

Also, Sakai Chemical Industry Co. and Teikoku Kako Co. have enforced their own anti-recession measures.

Reduction of the titanium dioxide business will shortly be the industry's common problem with reference to diversification of their operations.

Taken from
Japan Chemical
Week
March 7, 1977

DuPont gets 1 yr extension on TiO₂ wastes — The EPA has granted DuPont a one-year extension to discharge liquid acid wastes from its Edgewater, Del. plant into the Atlantic Ocean. The plant produces titanium dioxide used in white paint. Under terms OF THE PERMIT, WHICH EXPIRES November 13, 1976, DuPont will be allowed to dispose of 115 ml/gal. of waste at a site about 45 miles southeast of Delaware Bay. The EPA stipulates that the company find some other disposal method by November 1, 1978.

DuPont's ocean disposal had met stiff opposition from environmentalists who charged that shellfish might become contaminated and that pollution might spread to beaches. The company originally asked the EPA for a three year permit to discharge 125 gal. yr. (ChemWeek 11/26/75 p17)

The Dutch Parliament voted to tax chemical processes deemed offensive to environment.

The measure is actually an amendment to legislation that empowered the government to tax waste-disposal companies. Minor chemical producers objected to this tax, claiming that it represented an extra cost that would be passed along to them, while larger chemical producers having their own waste-disposal facilities would escape the extra expense.

The amendment was added to restore the competitive balance between large and small producers. But a spokesman for the Dutch Employers Federation says industry fears the process levy might force chemical companies to switch to other processes, incurring high investment penalties.

The law has been passed by the Second Chamber of Parliament and is expected to go before the First Chamber in September, where, sources say, approval is virtually certain.

Taken from chemical engineering July 7 1975

Spain's anti-pollution legislation introduced in 1972 has not been implemented because of lack of funds, according to under-secretary for the environment, Sr. Alfonso Fisenat. Addressing a meeting of industrial engineers, he blamed successive administrations which have failed to allocate sufficient public funds. Spain spends less than a half per cent of GNP on anti-pollution measures, compared with 2 per cent spent in most industrialized countries.

Taken from ECN
March 1977

Taken from E.C.N
April 1976

THANN & MULHOUSE
Le Havre (FRANCE)

TiO₂ storm brews over the Seine

With the first whiff of spring in Europe, thoughts of continental tourism officials turn gratefully to crowded beaches, holidaymakers and the rewards which a sandy coastline and generous climate can bring to a recession-ravaged national budget.

It is surely no coincidence that the first flush of bikinis should mark a renewed attack by authorities on marine disposal of ferrous sulphate, effluent from the sulphate-route to titanium dioxide and the dreaded "red mud" of the Mediterranean and other areas of coastal Europe.

Not that Le Havre is the Côte d'Azur but that's where the early action is. Thann et Mulhouse, one of Europe's largest sulphate route producers, is cur-

rently in the firing line following an order from the court of Rouen forbidding dumping TiO₂ wastes in the Seine estuary at Le Havre. The case has now gone to the State Council but the French company has already lost the first round with a decision by the disputed claims section of the Council not to suspend the Rouen court's order.

At Thann et Mulhouse, the order is being taken very seriously. M. Bonneau, plant manager, has said categorically: "If we must stop dumping we will be forced to close the plant and place 1500 jobs and 2 per cent of French foreign trade in jeopardy." Although these heavily-weighted numbers clearly refer to additional concern over the effect of plant closure on the

French paints industry, the alternatives to a stoppage are not inviting.

Treatment plant could cost FF130m., well beyond the resources of the company, and will take two years to build. Clearly seeking government financial aid for such a facility, Bonneau asks: "Does France want to keep a titanium dioxide industry or does it want to abandon it... this is the choice which faces us." The State Council is now considering its final judgement.

● Back in more familiar if equally murky waters, the case against Montedison's notorious ferrous sulphate disposals from its Scarlino TiO₂ plant has started at Livorno. Despite a postponement due to the illness of one judge, a decision could be handed down by Easter. Corsica is seeking pollution damages of FF45m from Montedison.

Montedison to phase out Spinetta TiO₂ production

SEVERELY restricted by the new Italian anti-pollution legislation but unable to anticipate similar pressures being brought to bear on its competitors Montedison has decided to close down the older of its two titanium dioxide plants at Spinetta Marengo, south-west of Milan, within 2-3 years.

One of the few land-locked plants in Europe, the Spinetta plant has avoided the attention which has focused at the company's other sulphate route plant at Scarlino, but unlike the latter its closure, together with the associated sulphuric acid plant, does not necessitate large-scale redundancies.

The workforce of about 500 men will be absorbed by expansions in production of hydrofluoric acid derivatives, fluorocarbons and peroxide products such as antioxidants and stabilizers already established at the Spinetta complex.

The closure is part of a plan to rationalize the company's TiO₂ production between Scarlino (design capacity 54 000 ton/year, but currently restricted to about 36 000 ton/year) and its new chloride route plant planned for Crotona in the south-east and due on-stream in 1979.

The new plant will have a capacity of at least 40 000 ton/year and the re-organization should allow an expansion of the current 90 000 ton/year total production to between 100 and 130 000 ton/year.

Scarlino Losses

Closure of the Scarlino plant is impossible, according to Montedison, because it would affect 2 000 workers in all, the plant being integrated with the sulphuric acid plant and in turn with the local pyrites mines, and there being no other production on the site.

But keeping the plant running is generating a L10 billion/year loss, according to the company, as a result of anti-pollution measures which amount to a L200 component of production costs. This is nearly a third of the L550/kg market price and this Montedison considers is hardly satisfactory even for North European producers who in most cases completely avoid waste treatment costs.

On top of the burden of treatment costs, the economics of the Scarlino operation is further distorted by the impossibility of reaching design capacity production rates. This is because the local authority (of the Regione Toscana), while granting the company permission to dispose of 2 600 ton/day of neutralized strong acids and gypsum in the open sea, interpret this limitation on a

day-to-day basis; dumping not carried out on one day because of weather conditions cannot be carried over to the next. Since dumping can only be carried out during calm weather, this effectively reduces the annual production by a quarter.

Hoping to overcome this problem, Montedison has recently been given permission to stockpile previously dumped gypsum (produced in the strong acid neutralization step) in addition to the 450 ton/day of ferrous sulphate and insoluble waste already stockpiled.

The 11 hectare plot which the company may use, however, will only be sufficient for 1½ years' gypsum waste produced at the rate of between 12 000 and 18 000 ton/year, but it may allow the company to achieve full production.

Uneconomic Recovery

Two waste treatment techniques introduced in 1972 at Spinetta Marengo, the roasting of ferrous sulphate to produce sulphur dioxide for acid production and the concentration of waste strong acids, have since become totally uneconomic.

In early 1973, however, when the Scarlino affair was erupting, Montedison announced that it would construct similar plants there before 1976. The fifth sulphuric acid line at Scarlino was constructed so as to receive a recycle stream of sulphur dioxide and acid evaporation equipment was acquired, but Montedison states that the plants were not feasible after the oil crisis.

[See article in ECN's Inorganics Supplement published with this issue.]

Only one other producer in Europe, Bayer, carries out ferrous sulphate roasting, but the company is in a unique position to utilize the iron oxide residues for pigment production and to supplement aniline residues for the same purpose.

The Spinetta plant releases its effluent into the river Bormida, a tributary of the Po, some 600 km. from the sea.

Montedison's problems at Scarlino, although sparked off by the complaints of Corsican fishermen, have been perpetuated by the local authorities which have adopted the most rigid attitude to control of the waste. The company may have been prompted to make its decision on Spinetta following the introduction earlier this year of Italy's first national water pollution control legislation; known as the Merli law, it has already been amended twice and its implementation postponed for one year, but as it stands, it proposes a rigid emission con-

trol system which has worried industrialists. Under the Merli law, regional authorities retain the right to impose their own requirements on industry.

The Merli law although concerned with all emissions into sea and rivers leaves the sea dumping of waste as a separate issue.

Local authority restrictions even before the passing of the Merli law had virtually necessitated the closure of Spinetta, but the new law has reinforced the position; the plant currently operates on a temporary permit.

Saddled with the tightest controls in Europe, Montedison has been supported by the Italian government in its efforts to persuade the EEC Commission that all European titanium dioxide producers should be subject to the same emission controls. In particular the government is adamant that the UK argument justifying the exploitation of open seas should not be accepted. It cites a report of the UK Royal Commission on Environmental Pollution which casts doubts on the effectiveness of the open sea dispersion techniques used by French and UK producers.

It points out that the EEC Commission objected to the original draft of Italy's new legislation because it anticipated public assistance for companies undertaking anti-pollution investments. A later compromise allowed the granting of state aids for a four-year period only, but domestic economic problems forced the Italian parliament to withdraw the L100 billion funding envisaged under this scheme.

Government spokesmen protest that other European countries are allowing investment rebates for anti-pollution facilities and Sweden (albeit outside the EEC) has subsidized these investments to the tune of 75 per cent. Coming from the heavily subsidized Italian chemical industry these complaints ring rather hollow.

Import Controls

It is hinted that if this argument is ignored by the Commission, Italy, and France, which is also having to adopt a rigid national policy towards titanium dioxide waste, may resort to import controls as a means of protecting their domestic industries.

The Italian government is also concerned about what it regards as a further distortion of competition; high levels of state assistance to industries carrying out pollution control investments.

Crotona

Montedison's Crotona plant will use chloride route technology developed jointly by the company and New Jersey Zinc during a six-year co-operation. Developments include refinements to the titanium tetrachloride production stage and the treatment of pigment.

Toxide under pressure on effluent disposal

THE Toxide group's French subsidiary, Toxide SA, is now coming under the same pressure as its rival, Thann et Mulhouse, to cut down on the discharge of titanium dioxide effluent into the English Channel.

Following complaints by fishermen and the city of Grand-Fort-Philippe, Jacques Gateaux, manager of Toxide's Calais plant, was last week charged with pollution by the administrative court at Lille.

This is the second complaint against Toxide this year. Last March, fishermen from Gravelines, near Dunkerque, asked the Lille court to apply antipollution laws to the Calais plant. Both complaints are seeking to cancel the authorization to double the plant's capacity.

Expanded twice since it started production in 1967, Toxide's plant at Calais now has a capacity of 60 000 ton/year. Efforts have already been made over the years to reduce its effluent—for instance, by changing its feedstock from wholly Australian ilmenite to "substantially" Sorel slag. But since 1970 local fishermen have been complaining of drastically reduced catches, and a rising incidence of the skin disease, necrosis, in their fish.

The Calais plant discharges an annual total of 200 000 cubic metres of sulphuric acid and 15 000 ton of ferrous sulphate into the Channel.

Although the fishermen are seeking a formal ban on further expansion, local antipathy has already caused Toxide to abandon its earlier ambitions for the Calais site.

At one time it was firmly destined to become the group's largest production plant in Europe, with a capacity of over 100 000 ton/year. But the emphasis for expansion has now switched to Huelva, where the affiliate Titano SA has just started its new plant.

Taken from E.C.N
November 19, 1976
TIOXIDE
Calais (FRANCE)

Taken from E.C.N 1976
MONTEDISON Spinetta (Italy)


Effluent problems delay Montedison TiO₂ project

MONTEDISON has delayed start-up of its 50 000 ton/year sulphate route TiO₂ plant at Scarlino, at the request of the regional Tuscan council.

Although start-up was originally scheduled for December 18, Montedison has been forced into the delaying measure following reports of heavy discharges of spent sulphate liquors from the plant.

Montedison has also agreed to admit a panel of experts nominated by the Tuscan council to its Spinetta Marengo TiO₂ plant, where a purification plant for the disposal of waste liquors produced at Scarlino is under construction.

The experts will evaluate performance of the purification plant and assess its potential in disposing of the Scarlino effluents.

Taken from ECN 
January 1972

TDI and TiO₂ problems rectified by Montedison

AFTER A series of delays, the start-up of the new Montedison toluene di-isocyanate plant at Porto Marghera is expected to begin again at the end of May.


Montedison has also commenced the waste disposal programme associated with the start-up of its new titanium dioxide plant at Scarlino. Following discussions on the programme with the regional authorities, Montedison has been granted a temporary operating permission.

Both plants were originally scheduled to start up last year, the TiO₂ unit in December and the TDI plant in the spring.

Gas Emission

In April last year, Montedison received temporary authorization for the commissioning of the TDI facilities, following a technical check by the authorities in March. Problems first emerged at the turn of the year with occasional emissions of ammonium chloride, a non-toxic gas. Fostered by public reaction against other pollution troubles in the area, reports of escaping gas from the Porto Marghera plant lead to widespread alarm.

The local authorities responded by ordering a suspension of operations until they considered the unit safe and a number of precautionary measures were taken. The suspensions began in February but 10 to 20 days later, after the introduction of these measures, temporary permission was given to re-start the unit.

Taken from EC N 
May 1972

TiO₂ Effluent Disposal

Meanwhile, Montedison has successfully commissioned the first two lines of its Scarlino titanium dioxide plant and begun barging operations to dispose of the waste ferrous sulphate in deep water. The company has evidently assured the regional authorities that it will be carrying out this operation in accordance with established practice in the USA and N. Europe.

At the same time, it has outlined plans for the adaptation of the pyrites-based sulphuric acid facilities associated with the plant to convert the ferrous sulphate effluent into ferrous oxide and sulphuric acid. Montedison already produces ferrous oxide in the existing sulphuric acid plant as a by-product, and operates pelletizing facilities. Plant adaptation is expected to be complete by mid-1973.


The modifications will resemble those made to the company's sulphate route TiO₂ plant at Spinetta Marengo. The facilities are now complete and Montedison is engaged on tests to establish optimum operating conditions.

Further TiO₂ capacity is expected to come on stream at Scarlino at the year-end, with the addition of a new 18 000 ton/year line to raise total capacity to 54 000 ton/year.

Montedison TiO₂ plant attacked again

MONACO has joined the massed ranks of Mediterranean countries lining up against the continued operation of Montedison's titanium dioxide plant at Scarlino, Italy.

Prince Rainier recently described Montedison's failure to control wastes from the plant as "scandalous." Marine life in certain areas of the Mediterranean is said to have been seriously affected, but the Italian government still maintains that Montedison is not in any position "to make 400 plant employees jobless."

Taken from EC N 
February 1973

Montedison TiO₂ plant faces closure

MONTEDISON now faces a Mediterranean protest lobby determined to close the company's 36 000 ton/year titanium dioxide plant at Scarlino, Italy. In protest against the marine dumping of effluent wastes from the sulphate-route TiO₂ plant, Corsican workers recently blockaded two ports in Corsica while demonstrators seized the Corsican Deputy Prefect.

Montedison dumps around 3 000 ton/day of TiO₂ plant wastes, containing round 20 per cent sulphuric acid, six per cent iron and small quantities of titanium, vanadium and chrome oxide together with ferrous sulphate wastes.

The company is now studying a new system of deep water effluent disposal but as a longer term solution has recently signed a contract with New Jersey Zinc, USA for an effluent-disposal unit at the plant site.

Montedison has previously detailed other plans for disposal of ferrous sulphate, involving the conversion of effluent into ferrous oxide and sulphuric acid. In May, 1972 the company stated that it planned to convert pyrites-based sulphuric acid facilities at Scarlino to handle the effluent by mid-1973.

But when Montedison announced the award of a contract to De Nora for a new interpass adsorption 600 ton/day

sulphuric acid plant at Scarlino in November, 1972 for early 1974 commissioning, the Italian company also stated that a second 250 ton/day furnace, using ferrous sulphate as feedstock, would be added "at a later date."

Montedison's latest contract to New Jersey Zinc now suggests that the company has acknowledged that ferrous sulphate re-use will not solve the problem entirely.

The company has now given an undertaking to the Italian Government to spend L9 000m. on solving pollution problems at Scarlino. Montedison states that it will commence operation of a ferrous sulphate re-cycling system similar to that in use at the company's Spinetta Marengo plant by the end of this year.

Sulphuric acid waste problems will be solved within three years, claims Montedison, when the New Jersey Zinc treatment plant comes into operation. The unit will convert 20 per cent dilute sulphuric acid wastes into 80-85 per cent concentrated sulphuric acid.

The issue of "the red scum" has now blown up into a major Mediterranean dispute and with the lucrative tourist season fast approaching, Montedison would do well to cut disposal levels within the next month or so or face closure of the TiO₂ plant.

Taken from EC N 
February 1973

ANNEX 9-3-2

ENVIRONMENTAL PRESSURE CONCERNING MONTEDISON

(MID. 73 JULY 76)

Dumping extension revives (TiO₂) dispute

MONTEDISON is in more trouble over marine dumping of wastes from its 36 000 ton/year sulphate-route TiO₂ plant at Scarlino, Italy.

Early this week, port authorities at Livorno, Italy announced that Montedison had been granted an 18-month postponement of the deadline by which it must stop dumping wastes from the plant in the sea near Corsica.

The news was greeted with unbridled anger from the Corsican populace and a series of marches through the streets of Ajaccio. A mysterious outbreak of fires also spread through the island.

Montedison dumps around 3 000 ton/day of TiO₂ plant wastes in the general area of the Ligurian and Tyrrhenian Seas.

The company, which has given an undertaking to the Italian government that it will spend L9 000m. in ending pollution from the Scarlino plant, has examined deep-water injection disposal of effluents and ferrous sulphate recycling as means of solving its problem.

Montedison plans to install a ferrous

sulphate re-cycling system at the plant by the end of this year. But sulphuric acid wastes will still be a problem for the next three years, until Montedison installs its planned New Jersey Zinc-designed treatment plant at Scarlino. The treatment plant will convert 20 per cent dilute sulphuric acid wastes into usable 80-85 per cent concentrated sulphuric acid.

France, Monaco and Corsica have all protested strongly on marine dumping of wastes over the past few months and Dick Taverner, the UK's independent labour member at the European parliament, has now urged the EEC Commission to intervene in the matter.

With the latest controversy blowing up at the present time, other members of the TiO₂ industry suggest that Montedison may have been better advised to close the plant, at least for the comparatively short period of the lucrative tourist season. Racing world TiO₂ demand and employment considerations have obviously dictated otherwise.

← Taken from E.C.N
mid 1973

Montedison ships seized:
(TiO₂) plant closed down

MONTEDISON has finally been forced to close down its titanium dioxide plant at Scarlino, Italy. The plant has been permanently under fire for the last year on the marine dumping of effluent wastes from the sulphate-route process and Montedison has had to face a wave of protests from many countries on the northern seaboard of the Mediterranean on the issue of the "red scum".

The situation was brought to a head last week when Scarlino's local magistrate, who has already lodged a suit against Montedison for pollution of the Tyrrhenian Sea, effectively broke the deadlock by simply ordering the seizure of the two ships used by the company for disposing wastes at sea.

Around 500 people were employed by the plant and Montedison is to appeal against the magistrate's action. The unemployment which plant closure would cause has been Montedison's major claim in defence of continued operation

in the past. However, the weight of Italian opinion now seems to be solidly against the plant.

Interviewed this week, magistrate Gianfranco Vignetta refused to revoke the seizure until harmful elements are removed from the wastes. He appears to have the backing of Tuscan regional authorities, who were told by Montedison this week that deep-water dumping of wastes was the only practical disposal method at present.

The plant's 500 workers are now on continuous assembly outside the site and further action on their part seems likely.

But the plant may have to remain closed until Montedison brings on its long-promised ferrous sulphate re-cycling system at Scarlino at the end of this year. The 36 000 ton/year plant supplied an estimated 25 per cent of Italian TiO₂ demand and Italian paint and paper makers can now be expected to launch a desperate search for material.

October
1975

Montedison to re-start
TiO₂ effluent dumping

MONTEDISON has just received permission from the Livorno port authorities to re-start marine dumping of effluent from its Scarlino titanium dioxide plant.

This move follows Montedison's successful development of new treatment methods. Acids formerly contained the effluent can now be neutralized and metallic residues, previously suspended in the liquid effluent, are now fixed in a chalky neutralizing agent.

Montedison was forced to suspend marine dumping in September last year when two ships used in the operation were seized by local magistrates. The plant was closed down for a short period but later re-opened at very reduced operating rates with effluent being treated at the plant site itself.

Permission to re-start dumping in the sea has been granted for a trial period of six months and Montedison hopes to build up production at Scarlino.

Taken from E.C.N
February 1974

Montedison closes Scarlino TiO₂
plant and halts effluent project

CURRENTLY showing all the classic signs of defeat over the "red scum" pollution issue, Montedison has closed down its 40 000 ton/year sulphate route titanium dioxide plant at Scarlino and laid off 400 workers for an indefinite period.

After a massive wave of protests from fishing and tourist interests forced the closure of the plant in 1973 when two ships used by Montedison for dumping ferrous sulphate waste at sea were seized by a local magistrate, the company has been neutralizing and storing its effluent on land.

A solution to the problem was due to come in the form of a major ferrous sulphate treatment plant, constructed in conjunction with New Jersey Zinc, at the end of last year. But the heavy cost of the treatment plant and running costs estimated at £6.5m. annually have led Montedison to abandon work on the project.

The company claims that all of the other 17 titanium dioxide plants in Europe are still dumping effluent, either at sea or on land, and adds that it is not economically possible to produce titanium dioxide at Scarlino while its competitors are not compelled to make similar anti-pollution investments.

Market observers say that Montedison has adopted a strong line on this point at meetings of RETIPE, the

organization set up by European TiO₂ producers to examine effluent treatment problems. And in defence of Montedison, it must be said that the only real initiatives on installation of large-scale effluent treatment facilities are coming from the US TiO₂ producers. American Cyanamid plans to start a major unit at its Savannah, Georgia, plant next month, for example.

Sources also expect Montedison to dig in its heels over the Scarlino issue and believe that this latest closure will be lengthy, running into months rather than weeks.

Closure of the Scarlino plant also threatens the related sulphuric acid and iron pellets plant, sold by Montedison to the state agency Egam two years ago. The plant supplies sulphuric acid to Scarlino, using pyrites mined in nearby Tuscan mines.

All the usual accoutrements of a Montedison dispute with unions are there—400 workers have occupied the TiO₂ plant in protest and unions are claiming that the company's action threatens a local workforce of 3 000. ● European TiO₂ markets are now experiencing the mildest of upturns as the spring house painting season approaches. But most producers expect the revival to be of a temporary nature, with demand flattening again by mid-year.

Italy

●285 651
Montedison has won its appeal in the red mud case, thanks to a new antipollution law rushed through the last parliament in its dying days. According to the new law, the charges brought against Montedison for discharging the Ligurian and Tyrrhenian waters with 3,000 m tons of titanium dioxide waste do not constitute a crime. The Merli law which came into operation in June supercedes all previous ones. Under this law, industries wishing to discharge wastes into coastal waters must first gain permission from the relevant port authorities, satisfactory evidence that measures have been taken against pollution.

The complex Merli law is an attempt to rationalize the present system of environmental controls and to reduce the present level of pollution 80% by the mid-1980s. Under the terms of the new law, control of the regulations has been withdrawn from the numerous and conflicting bodies and authorities invested with supervisory power in the past. It has been placed with a new interministerial committee. In future this committee will hand down the general and technical guidelines against pollution.

Chem Age 7/16/76 p16

Montedison cleared in
"red mud" case

THE "red mud" case against Montedison has ended with the acquittal of chairman Eugenio Cefis and other company executives. The company and its executives were being sued by Corsican interests who claimed that ferrous oxide dumping from the Scarlino titanium dioxide plant was damaging Corsica's fishing industry and tourist potential. Dismissing the charges, the Livorno court said it had taken into account a new Italian law authorising the dumping and applied it retrospectively.

Taken from E.C.N
July 1976

POLLUTION CONTROL IN JAPAN

In view of the situation, the Pollution Control Council was established in the Ministry of Health and Welfare in 1965. At the same time, The Environmental Pollution Control Service Corporation was created, and in the National Diet, the Special Committee for Countermeasures against Industrial Pollution was organized.

1967 - 1970

In 1967, the Basic Law for Environmental Pollution Control was enacted. The enactment of this law followed two years of Government studies intended to clarify the common principles and objectives and define how the administration of pollution control which was divided among several ministries should be coordinated so that overall preventive measures could be carried out by the government.

The problems of environmental pollution vary greatly from region to region. Therefore, this law provided for establishing a Council for Control of Environmental Pollution in each prefectural office and the Central Council for Control of Environmental Pollution in the Prime Minister's Office. As the result, local level government administration has been very positive in its activities to prevent environmental pollution.

Based on the fundamental law mentioned above, a series of supplementary laws, including the Air Pollution Control Law and Noise Regulation Law, were instituted. In addition, the 64th Extraordinary National Diet of 1970, commonly called the "Anti-Pollution Diet," passed as many as fourteen pollution-related bills including partial amendment to the Basic Law for Environmental Pollution Control, and in the same year environmental quality standards for carbon oxide, water quality and noise were established. In this way, Japan's environmental controls were conspicuously strengthened.

Since 1971

In addition to the improved legal pollution controls, nation wide demand for establishment of a central administrative organ to enforce positive environmental policies including those dealing of conservation of the natural environment gained momentum. For this reason, the Environment Agency and its adjunct organs, the National Institute for Environmental Pollution Research and the Training Institute for Environmental Pollution Control were established in 1974. The foundation was thus laid both for the promotion of environmental science research and for the training of environmental pollution control officials for local public organizations.

At the same time, the environmental pollution control ordinance has been instituted by all prefectural governments. The number of pollution control agreements concluded between local agencies and companies has been rapidly increasing since 1971. In 1974 alone, an estimated 7,000 such agreements were in effect.

Since the inauguration of the Environment Agency, additional new laws have been enacted or the existing laws have been amended. Thus, the basic preparations for the environmental protection system in Japan have been practically completed. From now on, the environmental protection policies of the government will place emphasis on the following points:

- Creation and strengthening of environmental and related standards.
- Strengthening of environmental pollution surveillance and control systems.
- Financing and subsidies for investment in environmental pollution prevention facilities.
- Implementation of compensation to sufferers of pollution-caused problems and illnesses.
- Promotion of policy for recycling industrial and general wastes.

(2) Cost and Effect of Environmental Pollution Prevention

With the improvement of environmental control administration the environmental abatement expenditures in the national budget continue to increase year after year. In the ratio of such expenditures to GNP, Japan assumes top place among major industrialized countries (Table 1). The environmental abatement budget of the government, which amounted to ¥83 billion in fiscal 1970, increased more than four times to ¥380 billion in fiscal 1975. The percentage to the whole General Account budget remains at approximately 2 percent since fiscal 1973.

Table 1. Comparison of National Environmental Abatement Expenditures

Country	Ratio to GNP (1971-75) (Unit: %)
Japan	3.0-5.5
U.S.A.	0.8
F.R. Germany	0.8
Sweden	0.5-0.9
Italy	0.4
Netherlands	0.04

Source: OECD, Economic Policy Committee

Pollution Control Legislations

(1) The Legal Structure

Since the enactment of the Basic Law for Environmental Pollution Control in 1967 many related laws have been legislated in quick succession. The classification of these many laws and their organizations in charge are presented in Appendix 1.

(2) Outline of Major Legislations and Environmental Quality Standards

*The Basic Law for Environmental Pollution Control***Objective**

This law is to promote the comprehensive policies to combat environmental pollution and thereby ensuring the protection of the people's health and the conservation of their living environment. For this purpose, this law clarifies the responsibilities enterprises and the central and local governments have to prevent environmental pollution and defines the basic requirements of pollution preventive measures.

Definition

The term, "environmental pollution", means any situation in which human health and the living environment are damaged by air pollution, water pollution, soil pollution, noise, vibration, ground subsidence and offensive odors which arise over a considerable area as a result of industrial or other human activities.

Main Provisions

- 1) The government determines environmental standards relating to air pollution, water pollution, soil pollution and noise. Preventive measures against environmental pollution aim at maintaining such standards.
- 2) Local governments carry out measures based on those enforced by the state.

- 3) The Prime Minister instructs the prefectural governor concerned to formulate preventive measures against pollution within the prefecture's specific region.
- 4) Enterprises bear whole or part of the expenses incurred to the central or local governments taking steps to control pollution originally caused by private enterprises. (Relevant legislation: Law Concerning 'Entrepreneurs' Bearing of the Cost of Public Pollution Control Works)
- 5) The central or local governments concerned takes necessary financial and tax-related measures for pollution preventive facilities to be installed by enterprises.
- 6) The Conference on Environmental Pollution Control (with the Prime Minister as president and the relevant State Ministers as members) is an adjunct organ in the Prime Minister's Office. At the same time, there is the Central Council for Control of Environmental Pollution which serves as an advisory organ in the Environment Agency. Local governments also establish their Pollution Countermeasures Deliberative Councils.

*The Air Pollution Control Law***Objective**

This law controls exhaustion of smoke and soot, etc. at factories and places of business, establishes the allowable limits for the exhaust gases of automobiles, and provides for liability without fault for compensation by the entrepreneur who has caused damage by air pollution.

Sulfur Oxides Emission Standard

The emission standard for SO₂ is calculated by the following formula:

$$q = K \times 10^{-3} H e^2$$

where

q : SO_x emission per hour from a given plant (Nm³)

K : Constant for the region of each plant given by Cabinet Order

He : The sum of actual stack height and smoke ascent height (m)

Toxic Substances Emission Standards

The emission standards for toxic substances other than SO_x are determined in density per m³ of exhaust gas according to the type of substances. The standards are uniform for all parts of Japan as seen in Table 2-3.

Effluent Yields Gypsum And Pure Water At Cyanamid's TiO_2 Plant

By Abel Banov

A FEW HUNDRED YARDS from the towers and reactors of American Cyanamid's huge titanium dioxide plant near Savannah, Ga., a white heron gracefully soars on the wind, scanning the cattail-lined pond below, waiting for the slightest break to herald the presence of fish.

The clear water of the pond is what remains of hundreds of thousands of gallons of spent sulfuric acid waste flowing from the plant each day, which was once pumped after removal of the suspended solids into the nearby Savannah River to be neutralized by its inherent alkalinity.

The clarity of the water, along with red-beaked, brown-coated marsh hens

that vie with the herons for sustenance from the pond, is a testimonial to the ingenuity and engineering skill of George Roberts, director of TiO_2 Research and Development, and his band of chemists and engineers. Their success in cleaning up the waste streams of spent sulfuric acid from the two sulfate titanium dioxide plants at the Savannah site is credited with keeping that portion running. They also designed the plant to accept the liquid effluent from the chloride process plant, and solved that problem as well.

Bleak Outlook Two Years Ago

Only two years ago, the situation was none too bright. Environmental officials from Georgia and the federal

government had told Truman Koehler, who heads the company's TiO_2 operations, that his discharge into the Savannah River had to meet the newly proposed federal water standards, ruling out ocean disposal as an alternative.

American Cyanamid, with a 100,000-ton-per-year TiO_2 plant sitting on the river's bank turning out three to three and one-half million gallons a day of problem liquid, had no place to put it at least not after the cutoff date set by environmental authorities. That meant a big investment was in jeopardy, and it also meant that the various user-industries—coatings, paper, and plastics—faced as they were in 1973 and 1974 with TiO_2 shortages, were threatened with the loss of a significant portion of a critical raw material supply. The prospect all along the line was grim.

A \$20 Million Project

After deep cogitation and soul-searching and numerous conferences at all levels of the company, including the topmost—a decision was made to convert the spent sulfuric acid into gypsum. Some \$20 million later, lime, aluminum, titanium and alkaline earths flows by pipe from the TiO_2 plant to the new facility, where, after reaction with calcium carbonate, it becomes gypsum and water fit for fish, frogs, alligators, and marsh hens—all of which reside there.

400,000 Gallons of the Most Concentrated Stream
The acid, has a very low pH. This comes from the production stage where titanium hydrate is precipitated, following the sulfation step. The second source is a weak acid coming from tanks where titanium hydrolysis is washed free of impurities. The pH is about 6.5. The third comes from cooling water—used in contact coolers, and because it has only limited exposure to acid, it has a relatively high pH of three to five. Lime is used to neutralize it completely. The first two types are alleged to have caused the trouble in the days when they were allowed to

run, via a settling pond, to react with the alkalinity of the swift Savannah River (pH of 6.8 to 7.8) on the outgoing tide.

Two Separate Streams

Now, the strong and weak acids are separated. The strong goes to a pond lined with an impermeable Hypalon membrane. The pond's working basin can handle 200,000 gallons roughly a day's off-load of spent liquor. Sufficient reserve capacity is available to handle 15 days output, allowing time to correct unexpected problems. The weak acid stream also has a large reservoir which holds up to seven days' waste liquid.

From the reservoirs, huge pumps feed the acid streams to the neutralization reactors, where limestone is added to form carbon dioxide gas, which will be sold, and a slurry of almost pure gypsum. The remaining acid and dissolved salts are separated from the solids by settling and filtration and are forwarded to a final neutralization reactor.

In the final reactor the waste is further neutralized with slaked lime to a pH of seven to eight; air is blown through it to oxidize the dissolved iron and to precipitate it and the other metals present as insoluble hydroxides.

The combined gypsum-metal hydroxides and water are pumped to a settling tank that resembles an oversized Olympic swimming pool capable of holding two-million gallons. Clean water is drawn from the top and pumped to the plant for reuse. The gypsum-slurry or magma settles to the bottom and is pumped to a filtration system.

The water from the thickener overflow is discharged to an effluent ditch, which takes it to a final neutralization step, where it joins with about 20 million gallons of cooling water, the third source of troublesome liquid, and is readied for final disposal.

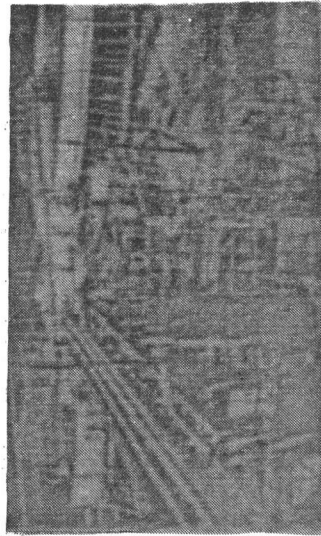
The final neutralized water is pumped to an effluent settling pond, able to hold 30 million gallons in its 25 acres, to remove the last traces of suspended solids.

The pond effluent overflows a dam through a metering device, which continuously monitors the flow and checks it for pH, and on into the Savannah River.

Big Expenditure Is Obvious

After seeing the operation in Savannah, as this writer did last month, it is not difficult to see the \$20-million investment. While Cyanamid has not published operating costs for the facility, informal discussions with several chemical engineers suggest that the effluent treatment will increase the manufacturing cost of TiO_2 by \$60 to \$80 a ton. Judging from the permits under which the TiO_2 industry is operating, the federal standards will be applied across the board by the middle of 1977. If this is the case, capital and operating costs of about this order of magnitude may be incurred by all TiO_2 suppliers.

It would appear that the industry has very little choice; either the capital is spent, and increased operating costs are incurred or capacity will be forced off-stream. Clearly, Cyanamid has decided to commit itself to continuing its supply of TiO_2 .



Cyanamid's answer to a federal demand... the means to clean water

Taken from I.S.K advertising brochure

From the time of starting the operation of our Yokkaichi Factory, in 1941, in order to prevent smoke pollution, we constructed a 185 meter high chimney, the tallest chimney in the world in those days, thus paying attention for the protection of regional environment. However, since about 1960, with the construction of new plants mainly of petrochemicals, Yokkaichi made a rapid progress as an industrial city which inevitably brought about pollution problems.

In 1954, with the production of titanium dioxide, the waste acid discharged therefrom was neutralized with lime and turned into gypsum. Further, from 1961, we have been recovering ammonium sulphate by treating waste acid, the first of its kind in the world.

Especially in 1970, at our Yokkaichi Factory, setting the target date of completion on September 30th for the purpose of establishing a completely pollution-free factory, all the workers welded together to prevent air and water pollution. As the result of constructing installation for thoroughly treating waste water and installation for turning wastes harmless, such as mist cottrell, tall chimney for collecting pollutants, concentration of waste acid by submerged combustion method, plant for neutralizing ferrous sulfate with sodium hydroxide, etc., our Factory has been highly evaluated and commended as a pollution-free factory.

Subsequently, year after year, we have continued investing positively in installations for pollution treatment and in 1974 we put to commission an installation for desulfurizing smoke from boiler chimney at the rate of 250,000 m³/hour, also installing filtration of waste water at the rate of 200,000 m³/day, thus we have invested a sum of 3 billion Yen for exhaust gas treatment while 5.1 billion Yen for treatment of waste water and wastes - equivalent to about 39% of the total plant investments. Thus, we are not only advancing a merely wholesome business activity, but we are also continuing intense endeavours every day to maintain clean environment and harmony with the society.

Sulfuric Acid (H₂SO₄)

We produce sulfuric acid for use in the manufacture of titanium dioxide, our main product, with raw material sulfur recovered from the oil refining industry. The production capacity is 15,000 tons per month. Further, the denser part of the waste sulfuric acid coming out of titanium dioxide plant is recovered as 62% H₂SO₄ and it is reused by recycling to our titanium dioxide plant. Capacity is 4,000 tons/month (62% concentration).

Gypsum (CaSO₄·2H₂O)

Gypsum is manufactured (16,000 tons/month) by treating the dilute waste acid discharged from our titanium dioxide plant with lime stone and slaked lime and sold to markets for gypsum board and cements.

Ferrous Sulfate (Fe·So₇·7H₂O)

Produced as by-product in the manufacturing process of titanium dioxide and recovered as ferrous sulfate whilst the remaining part is sold for water treatment as coagulating agent and for red iron oxide.

Sodium Sulfate (NaSO₃)

Utilizing ferrous sulfate by-produced from the titanium dioxide plant, Yokkaichi Chemical Co., Ltd. produce sodium sulfate by our technology. Capacity is 3,000 tons/month.

Uses: Detergent builder, pulp, glass, dye solvent

Ferrous - Ferric Oxide (FeO·Fe₂O₃)

These are by-produced and recovered from ammonium sulfate plant and sodium sulfate plant treating the ferrous sulfate and waste liquor discharged from titanium dioxide plant. The product may be used as raw material for the manufacture of iron.

Ammonium Metavanadate (NH₄VO₃)

Vanadium contained in ilmenite and slag is recovered in the form of ammonium metavanadate and sold as the raw material of the catalyst for manufacturing sulfuric acid, phthalic anhydride, and maleic anhydride, etc. and also to the manufacturers of ceramic pigment.

Sodium Silicofluoride (Na₂SiF₆)

By-produced in the manufacturing process of superphosphate and is sold as raw materials for glass, sodium fluoride, etc.

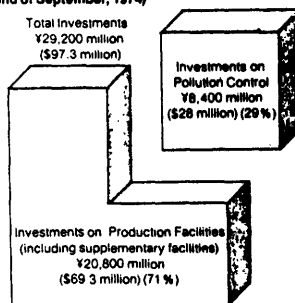
Sodium Sulfite (Na₂SO₃)

SO₂ gas exhausted from the manufacturing process of sulfuric acid is recovered as Na₂SO₃ and sold to the paper industry.

The substances discharged from the manufacturing processes tend easily to become sources of pollution, unless they are thoroughly treated

In 1970, a special program, called the "September 30 Campaign" was launched for purposes of converting the Yokkaichi plant to a completely pollution-free basis. Under the program, special equipment was installed to eliminate air contamination and to treat waste water. The construction involved a great number of technical difficulties, calling for the investment in the amount of ¥3 billion (\$10 million). The "September 30 Campaign" implemented by the whole Company accelerated the pollution control program to a great extent. In addition to the "September 30 Campaign," the Company has installed filtering facilities to turn waste water into a colorless and transparent liquid, exhaust gas desulfurizing facilities, reaction gas filtering facilities with the world's highest performance, facilities to completely incinerate organic wastes, and multilevel pollution control facilities at the titanium dioxide manufacturing plant—all in an effort to improve the environment in the Yokkaichi area. At the same time, projects to surround the plant with greenery were advanced in an attempt to improve purification of air and waste water. The amount required for the installation of those facilities during fiscal 1974 reached ¥2,624 million (\$8.7 million). Furthermore, the total investments for facilities and equipment at the Yokkaichi plant over the past 20 years amounted to ¥29.2 billion (\$97.3 million) of which ¥8.4 billion (\$28 million) or 29% was invested for pollution control facilities. Further efforts will mainly be exerted on exhaust gas denitrating, dust particle treating, deodorizing and waste water treating facilities. The Company has paid close attention to

Ratio of Investments on Pollution Control at Yokkaichi Plant Against Total Investment (As of end of September, 1974)



Taken from I.S.K Annual report 1974

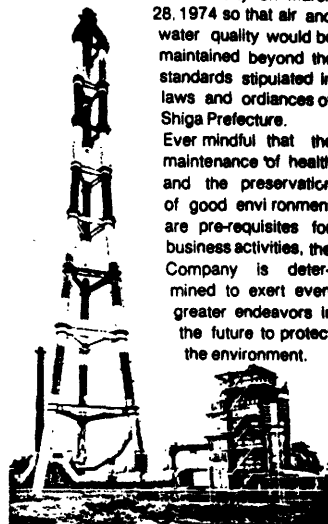
environmental protection in the area by erecting, for example, one of the world's tallest chimneys at the Yokkaichi plant to eliminate smoke pollution in 1941. In March 1975, the Company entered into the "Pollution Control Agreement" and "Disaster Prevention Agreement" with Yokkaichi City, committing itself to implement such measures to improve air and water quality beyond those standards set nationally and in the ordinances of Miye Prefecture.

At Kishu Copper Mine, waste water is discharged after complete purification through a "neutralizing cohesion settlement process" using automated equipment.

At the Central Research Laboratory, waste water is also discharged after it is made completely harmless through neutralizing settlement and oxygen aeration activated sludge process. The Laboratory entered into a "Pollution Control Agreement" with

Kusatsu City on March 28, 1974 so that air and water quality would be maintained beyond the standards stipulated in laws and ordinances of Shiga Prefecture.

Ever mindful that the maintenance of health and the preservation of good environment are pre-requisites for business activities, the Company is determined to exert even greater endeavors in the future to protect the environment.



← Taken from I.S.K advertising brochure

Growth of India's process industry

India joins the world market in industry growth. Problems exist, but India knows what to do about them

H. Holck-Larsen, Larsen & Toubro, Bombay, India

INDIAN PROCESS INDUSTRY joins the world in growth. Process industry expansion has been 2-3 fold from 1960 to 1975 while the chemical machinery industry expanded 13 fold. Consequently, facilities in India compare favorably with those the world over. However, India is not so well placed in the matter of raw materials. In addition, low productivity seems to a great extent, to annul the advantage of a low labor wage, i.e. wages are low with costs high resulting in low productivity.

THE INDIAN SCENE

Chemical plant industry growth developed from manufacture of simple equipment in the 1930s and importation of all other equipment to today's capability for process plant design, construction and operation which is comparable to other world areas (Table 1). Through hard work, intensive training and development of specialized facilities, India is now in a position to manufacture highly sophisticated equipment including, for example, nuclear reactors.

High costs, though, prevent Indian firms from participation in process plant projects around the world. Business occurs only under formation of consortiums of Indian and foreign firms or purely Indian firms. If process know-how is available, the approach is purely Indian. Or if technology is unavailable, the Indians act as sub-suppliers to main foreign contractors.

MARKET PARTICIPATION

To succeed in the international market, India sells itself as a reliable supplier of quality goods. This is matched by competitive prices and prompt delivery. Price is intimately linked with productivity, therefore, a conscious effort must be made to increase productivity or competition is unlikely. Delivery is most frequently jeopardized by availability of raw materials, particularly those which are imported.

India can manufacture almost any item no matter how stringent the design code, how close the tolerance or how severe the inspection. Raw materials and transportation facilities are the limiting restraints. India still lacks critical capabilities either totally or in part. For example, sufficient quantities of special alloy steels and some other critical materials are inadequate from local suppliers. Transportation is a setback because road and rail systems were designed for light loads and small equipment. Heavy construction equipment, massive items such as columns and oversized shipments exceed system capabilities.

India's most likely export markets are in the regions geographically close to home such as the Middle East and Far East. Such areas are also candidates for process plant sales. However, in most all cases, main contractors are American, Japanese or European, therefore, sales efforts must be directed towards New York, Tokyo or London.

Hardware prices are high and deliveries long. So long as these conditions prevail, India is better suited to export software: engineering and construction services. In both these fields, productivity of engineering staffs and skilled craftsmen, working abroad, have proved comparable with workers from other countries and India's success depends on its image as a reliable supplier of quality services.

TABLE 1—Index of industrial production
(Base: 1970 = 100)

	1971	1972	1973	1974	1975	1976 June
UNITED STATES						
Chem. Eng. Plant Cost.	105	109	115	132	146	152
Marshall & Swift Equip. Cost.	106	109	114	132	146	155
UNITED KINGDOM						
National Eco. Dev. O.E.	111	118	129	153	200	
Plant Cost.	110	118	140	165	220	260
Proc. Eng. Plant Cost.						
INDIA						
Wholesale Price Machinery & Transport Equip.	108	115	122	164	184	176

Taken from Hydrocarbon processing

WAGES AND PRODUCTIVITY

Indian wage scales are some of the lowest in the world. Surprisingly, however, Indian product prices are not competitive in international markets. This is especially true for "tailor-made" items such as process plant equipment. Three to four as much construction time is required by Indian fabricators as is required by their competitors. This together, with high machine tool costs makes India non-competitive in international markets. Note, however, that under controlled conditions of facilities and raw materials, an Indian worker, particularly a skilled worker, can perform as well as others.

Coordination of the work effort is the problem. Though Indian professional managers compare more or less with counterparts elsewhere, productivity suffers from equipment and material availability. Environmental and working conditions, non-availability of desirable materials, and consumables of the right quality at the right time increase total labor time by more than three times that in advanced countries. Work forces also suffer from the same situation such that in some major industries (fertilizer, chemical and petrochemical) staffs are often five to eight times what they are in similar plants elsewhere.

India has modern workshops but productivity is below standards of developed countries. Low productivity and high material costs (freight and lead time in material procurement) ruin their international competition. Manufacturers are now fully aware of these problems and are establishing time-standards and work measures to improve productivity—at all levels, from shop floor to chairman's office.

COST ESCALATION

No standard yet exists for updating equipment cost for a fully erected Indian process plant as is done in the United States or the United Kingdom (Table 2). However, wholesale price indices are available for machinery and transportation equipment made in India (Table 2).

TABLE 2—Comparison of cost indices
(1960 = 100)

	1965	1970	1975
Chemical & pharmaceutical machinery	373	840	1310
Engineering industry	213	226	260*
All Industries	154	181	205*

* Estimated

Although cost escalation is high in India—second only to that of the United Kingdom—there are indications that strict fiscal discipline and government control can reduce escalation in the future to levels similar to those in other countries. Initial evidence of the effectiveness of such measures is indicated by the latest data for the current year.

Abstracted from a paper presented as the Chaudhuri Memorial Lecture delivered in Delhi, India, Nov. 15, 1976.

About the author

HENNING HOLCK-LARSEN is chairman and chief executive of Larsen & Toubro (L&T) Ltd., Bombay, India. He went to India as a chemical engineer 40 years ago and founded L&T as a unique engineering organization concerned in India's national interest. Mr. Holck-Larsen was awarded the 1976 Ramon Magsaysay Award for International Understanding in recognition of his contribution towards India's technical modernization, industrialization and human concern.



Australia unsettled about minerals

Deciding on a mineral development policy is a major problem for the present Australian Labor government, under Prime Minister Gough Whitlam. Until a policy gels, development activities seem destined to remain virtually stagnant.

On the one hand, there is a deep-seated desire to develop the nation's vast mineral wealth in a way that will bring maximum benefits to its citizens, while on the other hand the government wishes to retain Australian control of ownership.

Foreign interests already control between 40 and 60% of Australia's minerals. Yet, the country's 13 million people will need additional outside funds (as well as outside technology) if they are to carry out future development.

Late last year, the Australian Parliament passed legislation establishing a Petroleum and Minerals Authority (PMA) with power to engage in exploration, production and sales of mineral and petroleum products, and to invest in mining ventures. This legislation was subsequently challenged by industry and four state governments.

On June 24 of this year, the Australian High Court rejected the legislation because it had not been properly presented to a joint sitting of both houses of Parliament. However, this court action still does not clear the decks for resumption of mineral exploration activity because Mineral and Energy Minister Rex Connor plans to reintroduce the PMA legislation to the Parliament.

The chairman of the Australian Petroleum Assn., David McGarry, reacted to Connor's decision by saying, "We are bottled up by the Minister who, in our opinion, is determined to nationalize the oil exploration industry by not allowing farm-outs, by controlling to the nth degree the issue of offshore permits and by creating an extremely difficult climate in which to work."

McGarry's reference to controlling offshore permits concerns the Submerged Lands Act. By this act, the federal government preempted control, from the state governments, of petroleum exploration and production by private companies. This legislation is also being challenged, in the courts, by the states.

Australia has been filling 70% of her demand for hydrocarbons from her own petroleum and gas fields, but this has been predicted to drop to 60% before long. Furthermore, proved reserves are sufficient for only about 12 years at present usage. . . .

Imports play major role

Even though Altona and the operations at Sydney are viable chemical processing operations, much of Australia's demand for CPI products is filled by imports.

Du Pont, for example, markets a range of imports, including nylon, photo-products wide stock, water gel explosives, acrylic fiber, acetal, Butacite (safety-glass interliner), Teflon, medium-density polyethylene, neoprene, cellophane, Lycra, spandex bulk-continuous filament for carpets and Dacron fiberfill. Du Pont admits that Australia's high protective tariff makes competition tough against local producers such as ICI, which manufactures nylon and other fibers, as well as polyethylene, locally.

Australia imports a lot of automotive pigment, although there are two local sulfate-process titanium dioxide plants. Du Pont thinks a world-scale chloride-process plant would be an interesting prospect, if sufficient chlorine were available. . . .

Taken from Chemical Engineering

October 13, 1975

Other processing prospects

Western Australia offers additional opportunities for development of chemical processing, based on resources other than gas and iron ore. These involve production of alumina (from bauxite), nickel matte, rutile, and copper, zinc. But the companies involved are working through various problems, such as: government agreement to the proposed amount of foreign participation, environmental impact, and a rapid inflation that threatens the competitive position of Australian products on the world market.

Among the possible projects: the Alwest A\$500-million bauxite and alumina operation slated for location 100 miles south of Perth, and the Pacminex A\$400-million project for the same type of development 20 miles north of Perth. Alwest, which is a joint venture of BHP and News, Ltd., quite likely may have Reynolds Aluminum as a U.S. participant. Pacminex is a joint venture of CSR Ltd. and the West Australian Hancock/Wright partnership.

Alcoa, meanwhile, is expanding production of its two alumina refineries in Western Australia, to reach an output level of 3.4 million tons by 1976.

Already a major producer of nickel (supplying about 8% of the world's need), Western Australia was expecting yet another project. This was the Agnew operation, planned to be under construction at a remote site 250 miles north of Kalgoorlie, sometime this year. Costing at least A\$300 million, it was designed to produce 20,000 tons/yr of matte containing some 70% nickel, with an ultimate expansion of production to 30,000 tons/yr.

However, in June, Agnew delayed the project indefinitely due to "the effect of inflation on capital and operating costs in relation to the international price of nickel."

Other mineral resources

Australian sources estimate that rich deposits of mineral sands containing rutile and zircon, located 100 miles north of Perth, will attract up to A\$100 million of investment within the next few years. One project is already operating (with five more expected, including beneficiating facilities at two). Added to the 500,000 tons/yr of output from fields south of Perth, these fields could raise the Western Australian mineral sands output to 1.5 million tons by the end of the decade.

Prospects for copper and zinc production hinge on exploration activity east of Geraldton, on the coast some 300 miles north of Perth.

Throughout Western Australia, as well as throughout the country as a whole, there is opportunity aplenty for future growth. It remains for the Australians to achieve the proper balance of political and economic factors that will encourage investment, opening the way for a rising, stable economy at home and for response to a continually expanding market demand overseas.

The author

Calvin S. Cronan is editor-in-chief of CHEMICAL ENGINEERING. He recently returned from a tour of the Far East, during which he spoke with chemical process industry executives. Cronan is a chemical engineering graduate of Northeastern University. After 2 years of industrial practice, he joined this magazine in 1962 and has been with it since then, except for a brief stint as chief editor of *Textile World*. He is a former chairman of Associated Business Publications' editorial committee, and is a director of AIChE.



European Communities – Commission

EUR 6024 – World TiO₂ industry projects and their environmental impact

Chimie Développement International, Paris

Luxembourg : Office for Official Publications of the European Communities

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Environment and quality of life series

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Such questions require an analysis of :

- the TiO₂ pigment industry and more specially the technical aspects dealing with the possible feedstocks
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 - the relative ore and chemicals consumption
 - the ore and chemicals prices
 - the main environmental constraints
- the cost of production of the main upgraded minerals this analysis has been carried out by taking into account
 - the processes
 - the locations
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- the potential market of upgraded minerals and the future development of the TiO₂ pigment industry
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