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### Publication Date

1981-12-01



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December 1981

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THE PRODUCTION OF TITANIUM FROM

ILMENITE: A REVIEW

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This work was supported by the Director, Office of Energy Research,  
Office of Basic Energy Sciences, Materials Sciences Division of the  
U.S. Department of Energy under contract # W-7405-ENG-48.

This manuscript was printed from originals provided by the author.

## ABSTRACT

The general principles for beneficiation of titanium ores are reviewed and the specific processes used in individual units in various countries are discussed. This is followed by a critical evaluation of various current and potential reduction methods for the production of titanium metal from the processed concentrates. Finally, the report outlines a research program for the development of a commercially viable alternative method for the production of titanium metal.

## 1. Introduction

The metal titanium is a strategically vital component in the defense and aerospace industries in the United States. Hence, a reliable source of the metal is a matter of national importance.

Titanium occurs in nature primarily as the oxide. The two principal ores are rutile, which is nearly pure  $TiO_2$ , and ilmenite, which is a mixture of titanium and iron oxides. These ores are converted to titanium tetrachloride,  $TiCl_4$  from which titanium is produced by reduction of the tetrachloride with magnesium or sodium. These processes are, however, extremely capital and energy intensive and the facilities require very long construction times. And while electrowinning of titanium appears to be promising, it has still to reach technical and commercial maturity. Thus, there is a major worldwide effort currently underway to develop alternative methods for the production of titanium metal.

The purpose of this report is to review the various current and potential methods for the production of titanium. After a brief survey of the occurrence and abundance of the resources, the principal methods for beneficiation of titanium ores are described in some detail. This is followed by a description of the methods being used for manufacture of titanium tetrachloride. A detailed review of the commercial processes for production of the metal then follows with a discussion of their merits and demerits. Some of the applications of titanium and its alloys are also described. Finally, a research program is outlined that is designed to lead to improvements in existing production methods and/or to a commercially viable alternative method for production of titanium.

## 2. Titanium Resources

Titanium is the fourth most abundant metal in the earth's crust and, more importantly, its ores are widely distributed throughout the world. In addition to the principal ores, rutile and ilmenite, titanium is also a constituent of other minerals, as Table 1 shows.

Table 1. Commercially Important Titanium Minerals

<u>Mineral Name</u>	<u>Composition</u>	<u>Characteristics</u>
Rutile	Nearly pure $\text{TiO}_2$ (90-95% $\text{TiO}_2$ )	Also occurs as the rutile allotropes, anatase and brookite
Ilmenite	$\text{FeO} \cdot \text{TiO}_2$ , minor amounts of magnetite or hematite; (contains 37-66% $\text{TiO}_2$ )	Iron oxide content varies depending on genesis of the ore, because above 600 °C ilmenite and hematite or magnetite are completely miscible. Partial desegregation occurs below 600 °C. Hematite or magnetite nearly impossible to separate if finely distributed
Titanomagnetite	$\text{Fe}(\text{Fe}, \text{Ti})_2\text{O}_4$	
Sphene	$\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$	
Perovskite	$\text{CaTiO}_3$	

Rutile and ilmenite are the only minerals of commercial significance. Of the other minerals, only sphene occurs in substantial quantities in the USSR [1]. Natural rutile because of its high  $\text{TiO}_2$  content and low impurity level, has historically been used to produce  $\text{TiCl}_4$ . However, the availability of natural

rutile has steadily decreased, and ilmenite and titanium-rich slags are increasingly used as feedstock in the U.S., Japan, and the U.S.S.R.

Table 2 lists world production of titanium ore concentrates [2]. Australia, which has some of the largest reserves of ilmenite and rutile, is the world's leading producer.

Identified world resources [3] of titanium are large, over  $330 \times 10^6$  tonnes of  $TiO_2$  in ilmenite and  $123 \times 10^6$  tonnes in rutile. Australia and Sierra Leone are credited with 46 and 36%, respectively, of the world total rutile reserves [4]. Ilmenite is more widely distributed. Norway, the U.S., the U.S.S.R., and Canada each hold approximately one-fifth of the world's ilmenite reserves [4]. U.S. reserves are estimated at  $28 \times 10^6$  tonnes of  $TiO_2$  in ilmenite and rutile, representing over  $14 \times 10^6$  tonnes of metal equivalent. Table 3 [5] gives the  $TiO_2$  contents of typical ilmenite deposits, as well as the oxide content after beneficiation.

### 2.1 Workability of Ore Deposits

The mineability of titanium ore deposits depends to a much greater degree on the subsequent steps involved in beneficiation of the ores, as compared with other metal ores. Primary deposits in which the ore must be crushed and ground for subsequent processing must have high Ti contents to be economically mined. Fine alluvial sands, on the other hand, are economically workable with  $TiO_2$  contents as low as 3%. The average composition of various titanium ores and slags are shown in Table 4 [6,7].

The beach sands found in Kerala and Tamil Nadu in India contain up to 80% ilmenite with an average  $TiO_2$  content of 57-61%, and are among the richest deposits in the world. West Australian ores contain up to 63% ilmenite and 10-30% rutile. Ore deposits in other countries have lower  $TiO_2$  contents. Table 5 compares the composition of ilmenite ores from various countries.



Table 2. World Production of Titanium Ore Concentrates

Country	Production in 1000 tonnes						
	1974	1975	1976	1977	1978	1979	1980
<b>1. Rutile</b>							
Australia	318.7	344.0	395.3	324.4	265.6	279.4	294.8
Brazil	0.15	0.1	0.05	0.13	0.37	0.37	0.4
India	5.8	3.6	3.6	6.0	14.5	12.0	12.0
Sierra Leone	-	-	-	-	-	10.7	41.2
South Africa	-	-	-	-	-	42.0	50.4
Sri Lanka	3.5	2.1	1.0	0.98	5.0	14.7	15.0
U.S.A.*	5.8	-	-	-	5.0	-	11.3(?)
U.S.S.R.	27.0	27.0	27.0	27.0	25.0	25.0	25.6
Total	360.95	376.8	426.95	358.51	315.47	384.17	450.7
<b>2. Ilmenite</b>							
Australia	831.5	1030.0	1001.8	1080.7	1237.7	1164.4	1309.2
Brazil	6.7	4.6	14.6	13.3	20.1	18.1	18.1
Finland	152.0	122.6	122.6	124.7	131.9	119.7	159.0
India	132.0	82.0	82.0	140.0	149.0	150.0	154.2
Korea	0.16	-	-	-	-	-	-
Malaysia	153.5	112.2	180.0	153.7	187.0	186.9	187.0
Norway	848.1	516.0	759.0	822.5	762.9	815.9	828.0
Portugal	0.3	0.2	0.4	0.4	0.3	0.27	0.23
Sri Lanka	78.0	62.99	55.8	34.1	85.0	55.4	57.2
U.S.A.	675.5	650.7	652.0	540.0	513.0	550.0	498.9
U.S.S.R.	305.0	325.0	380.0	400.0	400.0	450.0	450.0
Total	3182.76	2906.29	3248.2	3309.4	3487.6	3510.67	3661.83
<b>3. Ti-rich Slags</b>							
Canada (70-72% TiO <sub>2</sub> )	844.7	749.8	823.0	711.0	850.0	580.0	865.7
Japan (70-72% TiO <sub>2</sub> )	4.4	4.5	3.5	1.2	0.17	0.18	0.18
South Africa (85% TiO <sub>2</sub> )	-	-	-	-	90.7	330.0	326.6
Total	849.1	754.3	826.5	712.2	940.87	910.18	1192.48

\* Figures for U.S. production of rutile from 1974-1978 are available irregularly. After 1978 production was negligible.

Table 3. TiO<sub>2</sub> Contents of Various Ilmenite Deposits

	% TiO <sub>2</sub> in Ore	% TiO <sub>2</sub> in Concentrate	Identified Reserve (in 10 <sup>6</sup> metric tons)
Canada (St. Urbain)	35	37	200
Canada (Allard Lake)	32-40	43	20
USA (N.Y. State)	17	45	100
USA (Virginia)	18.5	44	5
USA (Florida)	0.5-3.0	63	180
Norway	17	43	250
Finland	13.5	44	50
India (Kerala)	20-40	59	100
South Africa (Umgababa)	5	49	20
Australia	30	50-65	15

Table 4. Average Composition of Titanium Ores and Slags (in percent)

Component	Rutile	High-TiO <sub>2</sub> Ilmenite	Low-TiO <sub>2</sub> Ilmenite	Titano- magnetite	Ti Slag
TiO <sub>2</sub>	96.3	57-61	39-50	8-11	70-85
FeO	<1	9-19	28-31	30-34	12-15
Fe <sub>2</sub> O <sub>3</sub>	<1	20-26	18-21	46-50	-
SiO <sub>2</sub>	0.6	0.5-2.0	1-9	1.5-4.5	5-7
Al <sub>2</sub> O <sub>3</sub>	0.9	1-2	1-4	3-6	8-10
CaO + MgO	1.4	1-2	2-5	1-3	5-7

Table 5: Typical Analyses of Various Ilmenite Ores (percent)

Component	Australia	India	Norway	Egypt
TiO <sub>2</sub>	54.8	60.6	43.8	40.6
FeO	24.0	9.6	34.4	24.4
Fe <sub>2</sub> O <sub>3</sub>	16.5	26.1	14.0	26.6
SiO <sub>2</sub>	1.1	0.8	2.2	4.44
Al <sub>2</sub> O <sub>3</sub>	0.75	0.5	0.56	3.25
MgO	0.18	0.5	3.73	-
CaO	0.01	-	0.19	0.25
MnO	1.3	0.4	0.30	-
Others	1.36	1.5	3.02	0.46

The steady depletion of the richer deposits has had the effect that in countries in Africa, and in the U.S. and the U.S.S.R. low-TiO<sub>2</sub> deposits are increasingly being exploited.

### 3. Beneficiation of the Ores

Depending on the composition of the ore, separation of TiO<sub>2</sub> from iron oxide and the siliceous gangue present is carried out by gravity, electrostatic, or magnetic methods. Pyrometallurgical (smelting) and chemical (flotation) separation methods are also used to refine the ores. Beach sands containing rutile and ilmenite are sufficiently fine and can be concentrated directly. All other ores must, however, be reduced to a size such that individual mineral particles in the ore are in effect liberated.

### 3.1: General Principles of Separation

The specific properties of ilmenite and rutile are advantageously employed to effect their separation from the siliceous gangue. Both minerals have high specific gravities (ilmenite, 4.5 - 5.0 g/cm<sup>3</sup>, depending on iron oxide content; rutile, 4.2 - 4.3 g/cm<sup>3</sup>), so that gravity separation is effective in separating the lighter gangue (siliceous gangue ~ 1.6 g/cm<sup>3</sup>). Further separation can then be carried out by electrostatic methods (ilmenite is surface conducting) or magnetic methods (ilmenite is magnetic, rutile is non-magnetic). Froth flotation is used to separate sulfide impurities. For reasons of cost, however, flotation is limited to the finer fractions.

Fig. 1 clearly illustrates the separation behavior of the individual mineral components in a titanium beach sand subjected to various physical separation methods [1].

In the case of other ores which must be crushed and ground, the large amounts of energy expended in these steps can be reduced by magnetically separating the gangue at each reduction stage. This results in some loss of the titanium mineral components (up to 10%), but the effective energy savings outweigh the cost disadvantages of mineral losses.

A general flowsheet for the concentration of a primary ilmenite - magnetite ore is shown in Fig. 2 [1]. The ore is crushed by jaw crushers and Symons crushers to < 20 mm. Grinding is carried out in rod mills which gives a product within a narrow range of particle sizes. Gravity separation utilizes either Humphreys spirals with a capacity of 1 - 1.5 tonnes per hour, or shaking tables. For electrostatic separation a rotor type separator is used in which the feeding rotor itself is the ionizing electrode at 40 - 80 kV. The feedstock must be completely dry and free from impurities such as alumina and iron oxide which adversely affect the separation efficiency. To separate

these impurities the feedstock is often treated with alkalis or acids and dried before electrostatic separation. A particle size range of 0.1 - 2 mm is most desirable with a separation rate of 1 - 2 tonne per hour per rotor. Magnetic separation is carried out in stages using high and low-field separators.

In the following paragraphs a brief description is given of various separation processes used in different countries [1,8,9].

### 3.1.1 Otanmäki, Finland

In Otanmäki 2000 tonnes of ore containing 28 - 32% ilmenite, 35 - 40% magnetite, 28 - 33% silicates and 1 - 1.5% pyrites are concentrated per day. The end product is a mixture of ilmenite and magnetite concentrates containing 44 - 45%  $TiO_2$  and 66 - 67% Fe, respectively.

The ore is successively crushed to < 34 mm and < 8 mm in Symons crushers. At each stage the nonmagnetic components in each size fraction are separated by a drum magnetic separator (12 - 15% separation by weight of the ore). The ore is then ground to < 0.2 mm in rod and ball mills with continuous closed circuit to the feed end of the mill. The power requirements for the grinding operation are given as 8.9 kWh/tonne.

The magnetic concentrate from wet magnetic separation contains in addition to 65% Fe and 3-5%  $TiO_2$ , approximately 0.85%  $V_2O_5$ . In a method unique to Otanmäki, vanadium is also recovered from the magnetite concentrate. The solid concentrate is mixed with approx. 5%  $Na_2SO_4$  and pelletized. After sintering at 1200 - 1250°C for 2-3 hours, the pellets are leached in hot water in a countercurrent reactor. The solution now contains 15-20 g/l of vanadium. The hot solution is treated with sulfuric acid to precipitate relatively pure vanadic acid.

The weakly magnetic concentrate fraction contains small amounts of

pyrites. To separate the latter the concentrate is first floated with xanthanate collectors. The ilmenite slurry is, in turn, scrubbed in a hydrocyclone and then floated successively with collectors (0.8 - 1.5 kg of anionic fatty acids per tonne of concentrate) and depressers (fluorides and fluorosilicates). During flotation the slurry must have a pH < 6.8.

A schematic flowsheet of the Otanmäki process is shown in Fig. 3.

### 3.1.2 Tahawus, New York, USA

The ores refined in Tahawus essentially contain 32% ilmenite and 37% magnetite with little or no impurities.

Fig. 4 is a flowsheet of the process. It is very similar to that used in Otanmäki. The ore is crushed and the low Ti fraction (5% TiO<sub>2</sub>, 10% Fe) is separated by a high-field magnetic separator. The crushed ore is ground in rod mills and the magnetite fraction is separated by a low-intensity machine. The finer fraction in the product is floated to recover ilmenite, while the coarser fraction is concentrated by tabling, magnetic separation, and flotation to separate ilmenite. The plant has a capacity of 5000 tonnes per day producing ilmenite concentrate with a TiO<sub>2</sub> content of 45%.

### 3.1.3 Tellnes, Norway

The Norwegian process is in all respects similar to those employed in Otanmäki and Tahawus as Fig. 5 shows [9a]. Magnetite is recovered by magnetic separation, ilmenite by froth flotation. Current production is about 800,000 tonnes of ilmenite concentrate per year.

### 3.1.4 Jacksonville, Florida, USA

The beach sands concentrated in Jacksonville have a low titanium content. In addition to rutile and ilmenite, however, the sands also contain considerable

amounts of monazite and zirconite. The heavy mineral component of the sands is about 4%. The plant concentrates 2.6 million tonnes per year to recover 40,000 tonnes of ilmenite, 6,500 tonnes of rutile, 11,000 tonnes of zirconia, and significant quantities of monazite.

As shown in Fig. 6 [1], the process differs from those described above. The beach sand is fed to a Humphreys spiral to separate the heavier mineral components. The heavy mineral concentrate is dried and then passed into an electrostatic separator to recover ilmenite and rutile. The latter are, in turn, separated from each other by magnetic methods, since rutile is non-magnetic. The residue from the electrostatic separator is then fed to a series of magnetic separators to recover zircon and monazite.

### 3.2 Pyrometallurgical Methods

As mentioned earlier, naturally occurring ilmenite ores contain varying amounts of iron oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . At high temperatures Ti can partially replace Fe in both hematite and magnetite to form a range of solid solutions terminating at  $(\text{Fe,Ti})\text{O}_3$  and  $(\text{Fe}_2\text{Ti})\text{O}_4$ . Both solid solutions tend to break down below  $600^\circ\text{C}$  to form hematite and ilmenite, and magnetite and ilmenite. Weathering also causes the ilmenite structure to break down leaving finely dispersed particles of titanium and iron oxides. Typical deposits of this kind are found near Lake Allard in Canada, Taberg in Sweden, and Abu-Ghalaga in Egypt.

Since the iron and titanium oxides are in solid solution, such ilmenite ores cannot be separated by mechanical methods. Allard Lake ore, for example, is concentrated by a smelting process, the Sorel process, to separate titanium oxide from the iron oxides. In the Sorel process [9-10a] crushed Lake Allard ore (< 50 mm) after beneficiation is

mixed and ground with coke, and the whole mass smelted at 1560°C in an electric furnace. The greater part of the iron content of the ore is obtained as essentially titanium-free metallic iron (see Table 6). The remaining slag contains about 72% TiO<sub>2</sub> together with other oxides (Table 6). A major problem during operation is that at the smelting temperatures the Ti-rich slag is chemically very aggressive towards most structural materials. The process has, therefore, only been used to a limited extent. The Sorel plant smelts 5,500 tonnes of ore per day with a coke consumption of 900 tonnes (low-ash anthracite) to produce 2,330 tonnes of TiO<sub>2</sub>-rich slag and 1,650 tonnes of metallic iron. The process flowsheet is shown in Fig. 7.

In 1978 a plant was set up to manufacture TiO<sub>2</sub>-slags in Richards Bay, South Africa, according to the Sorel process. In the Richards Bay operation heavy mineral sands are converted to a slag with > 85% TiO<sub>2</sub>. The plant has a capacity of 400,000 tonnes per year [9].

The inherent difficulties associated with high temperature smelting, as in the Sorel process, have led to the development of alternative methods in which the iron oxides are reduced at lower temperatures, 1150-1300°C. One such method [11] employs CO as the reducing agent to separate TiO<sub>2</sub> from iron oxide. The ore is mixed with coke (2%) and Na<sub>2</sub>SO<sub>4</sub> (15%) and reduced with CO at 1100°C. This method has been developed for beneficiation of Egyptian ilmenite from Abu-Ghalaga.

#### 4. Conversion of Ilmenite Concentrate

The greater part of titanium ore production is still employed in the manufacture of TiO<sub>2</sub> for use as pigment material. Less than 20% of the ore feed stocks consumed in the U.S. is used for metal production, and an



Table 6. Typical Analyses of Materials in the Sorel Process (percent) [1]

Component	Ore	Slag	Metallic Iron	Refined Iron
Ti			Trace	-
TiO <sub>2</sub>	34.8	71.9		
Fe	40.3		98.05	98.51
FeO		8.9		
V	0.16		-	-
V <sub>2</sub> O <sub>5</sub>		0.52		
Mn	0.14		Trace	Trace
MnO		0.19		
Cr	0.08		0.05	0.08
Cr <sub>2</sub> O <sub>3</sub>		0.25		
Cu	0.02			
Ni	0.02			
C			1.13	1.19
S	0.32	0.22		0.04
CaO	0.48			
MgO	2.9	5.2		
Al <sub>2</sub> O <sub>3</sub>	2.8	6.2		
Si			0.08	0.015
SiO <sub>2</sub>	3.4	5.7		
P			0.03	0.03
P <sub>2</sub> O <sub>5</sub>	0.015			

even smaller part is used for production of ferrotitanium.

The principal step in the production of the metal is conversion of the ore concentrate to  $TiCl_4$ . As natural rutile becomes progressively scarcer, synthetic rutile manufactured from ilmenite will become a more widely used feedstock. Direct reduction of ilmenite to iron and  $TiO_2$  is sluggish and therefore unattractive. Thus, the ore is generally refined to produce synthetic rutile, and although direct chlorination of ilmenite has been attempted, it has not been successful. Titanium-rich slags, on the other hand, can be chlorinated directly.

Since the processes for manufacture of synthetic rutile are in many respects similar to those for the manufacture of  $TiO_2$  for pigment use, a brief description of the latter is also given:

#### 4.1 $TiO_2$ - Pigment Material from Ilmenite Ore

Currently, there are two main processes employed for the manufacture of  $TiO_2$  for pigment:

- a) The sulfuric acid process in which ilmenite is dissolved in the acid and the titanium is precipitated as the oxyhydrate,  $Ti(OH)_4$ . The latter is thermally decomposed to  $TiO_2$ .
- b) Conversion of  $TiCl_4$  to  $TiO_2$  in the presence of air and hydrocarbons or steam.

##### 4.1.1 Sulfuric Acid Process

The process flowsheet is shown in Fig. 8 [9]. The ilmenite concentrate is digested with a slight excess of concentrated sulfuric acid ( $H_2SO_4/TiO_2$  - ratio  $\approx 1.2$  - 1.8) and then diluted with  $H_2O$  or recycled dilute acid. The acid concentration is about 70 - 96%. Superheated steam or hot air is blown in and the bath temperature is raised to 120 - 180 °C, thereby forming a thick sludge, or, in the case of hot air, a

porous cake is formed. After the conversion is complete the temperature is raised to 220 - 250 °C for a short time to increase product yield. The sludge/cake is dissolved in water or dilute acid. To prevent premature hydrolysis of titanium the temperature and the concentration of titanium are maintained at low levels, while coprecipitation of iron is avoided by reducing Fe(III) to Fe(II). This is carried out by suspending baskets of scrap iron in the bath. The solution is purified by filtration, or by sedimentation. These operations are aided by the addition of flocculants, or by forming small quantities of elemental sulfur or sulfides by passing SO<sub>2</sub> or H<sub>2</sub>S through the solution. Most of the iron is recovered as FeSO<sub>4</sub>·7H<sub>2</sub>O, which crystallizes on cooling.

The purified solution, still containing 10-20% iron (relative to titanium), is hydrolyzed by heating. Titanium precipitates as the oxyhydrate, Ti(OH)<sub>4</sub>, which is separated by filtration. The oxyhydrate is decomposed to TiO<sub>2</sub>. The filtrate contains large amounts of FeSO<sub>4</sub> in acid solution. A small part is recycled to the process, but the disposal of FeSO<sub>4</sub> presents a significant problem.

The pigmentation properties of the TiO<sub>2</sub> product depend primarily on the hydrolysis conditions and on the subsequent decomposition conditions. Various methods [9] have been used to influence the hydrolysis conditions by the addition of suitable nucleation agents.

#### 4.1.2 Conversion of TiCl<sub>4</sub> by Hydrolysis

The conversion of TiCl<sub>4</sub> to TiO<sub>2</sub> is of no interest for the manufacture of the metal. For pigment manufacture, however, the conversion is carried out by reacting a mixture of air and gaseous TiCl<sub>4</sub>, obtained from various

sources, with steam or gaseous hydrocarbons. The reaction must be very carefully controlled to obtain a  $\text{TiO}_2$  product that can be used to manufacture high-quality pigment. Pigment quality depends primarily on the allotropic modification of  $\text{TiO}_2$  (rutile has a higher refractive index than anatase), grain size, and impurity content.

#### 4.2 Production of Synthetic Rutile

As noted earlier, the manufacture of titanium metal requires  $\text{TiCl}_4$  as feedstock. Titanium tetrachloride is produced by chlorination of natural or synthetic rutile. The latter is, in turn, produced by complete or partial reduction (to  $\text{FeO}$ ) of the iron oxide in ilmenite. Attempts have also been made to chlorinate ilmenite directly, but without much success. Selective chlorination of ilmenite has also been tried [5].

##### 4.2.1 The Western Titanium Process

The Western Titanium process [12] involves complete reduction of the iron oxide content of ilmenite to metallic iron which is then separated as  $\text{Fe}(\text{OH})_3$ . Fig. 9 shows the flowsheet of the process.

Ilmenite ore is mixed with non-caking coal and heated in a rotary kiln. The iron oxide content of the ore is completely reduced to metallic iron, a part of the  $\text{TiO}_2$  is also reduced to  $\text{Ti}_2\text{O}_3$ . The reduction is carried out at a temperature  $>1200^\circ\text{C}$  which prevents both slag formation and any substantial sintering of the reaction products. The reduced ilmenite is agitated in aerated 1.0 - 1.5%  $\text{NH}_4\text{Cl}$  solution. Iron is dissolved and diffuses to the surface. The finely precipitated  $\text{Fe}(\text{OH})_3$  is separated by countercurrent washing in hydrocyclones. The aerated synthetic rutile contains approximately 3.5% Fe (total) and 1.6% Mn. It is given a mild acid leach (2% W/W  $\text{H}_2\text{SO}_4$ ) to dissolve the iron and manganese. The leached

pulp is washed in dewatering tanks, then filtered and dried. Table 7 gives the composition of the ilmenite feedstock and the final product. The plant has a rated capacity of 45000 tonnes per year of synthetic rutile and has, in fact, operated near capacity. It produced 42707 tonnes of synthetic rutile from June 1977 through June 1978.

Table 7. Typical Analyses of Materials in the Western Titanium Process (percent)

Component	Ilmenite Feedstock*	Synthetic Rutile Product
TiO <sub>2</sub>	59.6	92.8
Ti <sub>2</sub> O <sub>3</sub>	-	10.0
Fe <sub>2</sub> O <sub>3</sub>	15-29	2.1**
FeO	5-18	
MnO	1.1-1.2	1.0
Al <sub>2</sub> O <sub>3</sub>	0.6-1.2	1.1
SiO <sub>2</sub>	1.2	1.2
Free Silica	0.01-0.1	-
ZrO <sub>2</sub>	0.4-0.8	0.15
V <sub>2</sub> O <sub>5</sub>	0.12-0.16	0.20
Nb <sub>2</sub> O <sub>5</sub> , (Nb <sub>2</sub> O <sub>3</sub> )	0.17-0.22	(0.20)
Cr <sub>2</sub> O <sub>3</sub>	0.08-0.16	0.08
P <sub>2</sub> O <sub>5</sub>	0.06-0.20	-
CaO	0.01	0.03
MgO	0.18-0.26	0.30
S	0.25	0.30
P	-	0.02
C	-	0.30
Moisture	0.2	-

\*based on Capel Secondary and Eneabba Secondary ores  
 \*\*refers to total iron

#### 4.2.2 The Summit-Tiron Oceanic Process

The process, shown in Fig. 10 [5], is essentially similar to the Western Titanium process. The iron oxide content of ilmenite is completely reduced to metallic iron by non-caking coal in a rotary kiln. The reduced ilmenite is agitated in aerated  $\text{FeCl}_3$  solution to dissolve metallic iron as  $\text{FeCl}_2$ .  $\text{TiO}_2/\text{Ti}_2\text{O}_3$  is filtered off and the filtrate solution oxidized, partly to regenerate  $\text{FeCl}_3$ , which is recycled, and partly to form  $\text{Fe}(\text{OH})_3$ , which is separated. The  $\text{Fe}(\text{OH})_3$  contains large amounts of chloride and cannot be used to recover metallic iron. Thus, it presents a significant disposal problem. Separation of the chloride impurity is, however, an expensive but necessary step. The final product is high-grade synthetic rutile, as Table 8 shows. A large scale plant with a capacity of 20,000 tonnes per year is operating near Montreal.

Table 8. Typical Analysis of Synthetic Rutile from the Summit-Tiron Process (percent)

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$\text{TiO}_2$	94.0	$\text{Cr}_2\text{O}_3$	0.1
FeO	2.0	MgO+CaO	0.7
$\text{SiO}_2$	0.5	$\text{P}_2\text{O}_5$	0.1
$\text{ZrO}_2$	0.2	S	0.02
$\text{Al}_2\text{O}_3$	1.7	Mn	1.3
$\text{V}_2\text{O}_5$	0.15	Sn	0.05

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#### 4.2.3 The Murphoyres Murso Process

In this process (Fig. 11) [13], developed in Australia, synthetic rutile is produced by an oxidation-reduction method slightly different

Table 9. Identified World Capacity for Production of Synthetic Rutile [14, 23]

Process Type	Company	Location	Capacity Tonnes
Iron reduced to metal then separated chemically and physically	AMC/Western Titanium	Capel, Australia	52,000
Iron reduced to ferrous state, chemically leached	Ishihara-Sangyo Kaisha	Yorrich, Japan	48,000
	Malaysian Titanium	Lakat, Malaysia	54,450
	Kerr McGee Chemical	Mobile, Alabama	90,700
	Taiwan Alkali	Taiwan	30,000
	Dhrangadhra Chemicals	Sahupurasaa, India	30,000
			395,150

from the ones described above. The core of the process consists of reducing the iron oxide content of the ilmenite ore to the ferrous state, FeO. This is carried out in a fluidized bed reactor in a reducing air-fuel oil mixture. The reduction is completed in the second stage by means of hydrogen. The product is leached in 20% HCl at 108-110°C to precipitate FeCl<sub>2</sub> which is separated and calcined in air at 850°C to regenerate HCl and a saleable grade of Fe<sub>2</sub>O<sub>3</sub>. A typical analysis of the synthetic rutile product is 96% TiO<sub>2</sub>; 1.5% Fe<sub>2</sub>O<sub>3</sub>; 0.07% MnO; 0.08% MgO; and 0.05% V<sub>2</sub>O<sub>5</sub>.

Most other large-scale plants produce synthetic rutile by processes essentially similar to one of those described above [3,5]. The iron oxide content is reduced to the ferrous state and is separated by HCl, or H<sub>2</sub>SO<sub>4</sub>

as in the Ishihara-Sangyo Kaisha (Japan) process. The resulting iron sulfate, which has no commercial value, presents significant disposal problems. Other plants are located in Malaysia, the U.S., Taiwan, and India (Table 9).

#### 4.2.4 Other Processes

A different approach [15] to preparing synthetic rutile from ilmenite involves leaching of the ore directly after roasting. No reduction of the iron oxide is necessary. In this method the roasted ore is leached with dilute  $H_2SO_4$  under pressure and at 250-335°C to yield a synthetic rutile with > 90%  $TiO_2$  and < 0.5% Fe. In a variation of this approach [16] the ore can be leached with 20% HCl at 70-110°C to yield synthetic rutile. The major problem seems to be the disposal of large quantities of iron salts. Ilmenite can also be sulfidized with  $H_2S$  at 1000°C and the iron sulfide separated by leaching and boiling dilute HCl [17]. In another method ilmenite is reacted with nonaqueous  $H_2F - NO_2$  azeotrope at 52°C to dissolve titanium, while the iron precipitates [18].

#### 4.2.5 The Chlorine Technology Process

This is a newer process developed in Australia. The process involves selective chlorination of ilmenite. As shown in Fig. 12 [5], a mixture of ilmenite and coke is roasted in air. The roasted ore is chlorinated under reducing conditions in a fluidized bed reactor. Fe is volatilized as  $FeCl_2$  which is oxidized to recover chlorine and  $Fe_2O_3$ . The chlorine is recycled to the chlorinator. By carefully controlling the reaction conditions, high-quality synthetic rutile can be obtained. Despite extensive pilot-plant tests, no commercial plant based upon selective chlorination has been built to date [14].

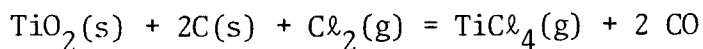


In another variation [19] the iron is separated by chlorinating the ore-coke mixture with hydrogen chloride at high temperatures. Most of the iron can then be dissolved by leaching with dilute acid.

Most of these methods for production of synthetic rutile are still in the developmental stage. There is relatively little large-scale operating experience for the processes that are in commercial operation. Whether the newer processes will achieve commercial break-through will depend on such factors as plant costs, ecological considerations, and raw material availability. There is no question, however, that development of commercially viable processes for production of synthetic rutile from ilmenite will be increasingly important in the future, not only for the production of Ti sponge, but also for the manufacture of  $TiO_2$  pigments.

## 5. Production of Titanium Tetrachloride

Titanium tetrachloride is at present produced by chlorination of natural rutile, according to the reaction



Increasingly, however, synthetic rutile produced from ilmenite, and titanium-rich slags are being used as feedstock. Direct chlorination of ilmenite has also been attempted with limited success.

### 5.1 Chlorination of Rutile

#### 5.1.1 Batch Process

In one of the earliest processes developed by the Titanium Metals Corporation of America [20], rutile sand is mixed with petroleum coke and coal tar as binder. The mixture is heated to remove volatile materials and the resulting product is briquetted. The briquettes are fed to the

chlorinator (Fig. 13). The reaction starts at 700°C in the presence of chlorine. During the reduction-chlorination reaction heat is evolved and the temperature rises to 1000°C. The gaseous reaction product contains  $\text{TiCl}_4$  (b. pt. 136°C), CO,  $\text{CO}_2$ , excess  $\text{Cl}_2$  and small quantities of volatile chlorides, (Fe, Si, Zr, Al, V, C, S). It is passed through a dust collector to remove particulate matter and the  $\text{TiCl}_4$  is condensed in a spray condenser by maintaining a counter current spray of cooled  $\text{TiCl}_4$  liquid. Since the impurities in rutile are also chlorinated, the  $\text{TiCl}_4$  product contains both non-volatile chlorides as a fine dust, and volatile chlorides, which distill over and condense to dissolve in liquid  $\text{TiCl}_4$ , or from a fine suspension, if insoluble. The crude tetrachloride is purified by sedimentation and filtration, followed by  $\text{H}_2\text{S}$  treatment to remove vanadium, and fractional distillation to separate the volatile chlorides. Effective separation is achieved by reboiling and refluxing to obtain fractions with different boiling points.

Typical analyses of crude and pure  $\text{TiCl}_4$  are given in Table 10 [21].

#### 5.1.2. Fluidized Bed Chlorination

Most modern plants employ fluidized bed chlorination [22,23]. This has the inherent advantages of good heat transfer properties, excellent gas-solid contact, faster reaction rates and, therefore, high productivity. It also eliminates the need of the feed preparation step since the rutile-coke charge does not have to be briquetted, and the presence of impurities such as Ca, Mn, Mg does not affect the process adversely. These elements form nonvolatile chlorides which tend to coat the surface of the briquettes [24]. By making suitable inert additions to the charge, it is also possible to chlorinate  $\text{TiO}_2$ -rich slags containing up to 6% CaO + MgO.

Table 10. Typical Analysis of Titanium Tetrachloride

Component	Crude	Pure
TiCl <sub>4</sub>	96-97%	> 99.9%
<u>Impurities (ppm)</u>		
Fe	50	< 30
V	1800-1900	< 100
S	30-150	10-80
Si	250	< 100
Cl	1000-3500	100-150
Non-volatile residue	1000-6000	None

Chlorination is generally carried out at 1100-1200°C in a silica-lined reactor. Once the reaction has started external heat input is no longer necessary because the reaction is exothermic. As in the batch process, TiCl<sub>4</sub> vapor is evolved with CO, CO<sub>2</sub>, unreacted Cl<sub>2</sub>, and other chloride impurities. The condensation and purification of TiCl<sub>4</sub> is essentially similar to that employed in the batch process. However, the product yields are slightly higher: Cl<sub>2</sub> > 95%, TiO<sub>2</sub> > 90%.

## 5.2 Chlorination of Other Charge Materials

### 5.2.1 Titanium Oxycarbide and Carbonitride

The reduction of rutile with coke at 1200-1400°C in the electric furnace often produces nitrogen-containing titanium oxycarbides, Ti(O,C,N).

Ti(O,C,N) converts to  $TiCl_4$  not much differently from rutile, but the reaction occurs more rapidly. Unfortunately, this advantage does not outweigh the expensive rutile-coke reduction step [22].

### 5.2.2 Ti-Containing Slags

$TiO_2$ -rich slags can be chlorinated directly in a fluidized-bed reactor to produce titanium tetrachloride [25-27]. The main problem, however, is the presence of large quantities of other oxides such as MgO and CaO. These oxides form non-volatile chlorides that adversely affect the chlorination process. Thus, flux additions are kept to a minimum possible in ilmenite smelting plants where the  $TiO_2$ -rich slags will be subsequently chlorinated [26,27]. For example, a slag containing 59%  $TiO_2$ , 32%  $Ti_2O_3$ , and only 0.09% MgO + CaO has been successfully smelted, although temperatures around 1700°C are necessary [27].

Intensive research efforts are currently underway in Australia, Japan, and the USSR to produce even higher quality  $TiO_2$ -rich slags suitable for chlorination.

### 5.2.3 Direct Chlorination of Ilmenite

Direct chlorination of ilmenite is possible; however, the large amounts of  $FeCl_3$  that are also produced present significant separation and disposal problems. To date the process has not been demonstrated on a commercial scale. OREMET, USA is probably closest of all worldwide efforts to commercial realization of a direct chlorination process [28].

Chlorination can be carried out without difficulty in a fluidized bed reactor. An excess of chlorine is maintained throughout the reaction to prevent the formation of non-volatile  $FeCl_2$  which tends to clog the system.

The ilmenite feedstock should be low in Mg and Ca for the reasons described earlier. The reaction product contains, in addition to  $\text{TiCl}_4$ , large quantities of gaseous  $\text{FeCl}_3$ , which is separated by one of the following methods [28]:

- a) The  $\text{TiCl}_3 + \text{FeCl}_3$  mixture is sprayed with cooled liquid  $\text{TiCl}_4$  and  $\text{FeCl}_3$  forms a fine suspension in the liquid. It is filtered off and the gas now contains very little  $\text{FeCl}_3$ .
- b) The gas is cooled to about  $15^\circ\text{C}$  above the sublimation point of  $\text{FeCl}_3$  and precisely regulated liquid  $\text{TiCl}_4$  is injected to precipitate nearly pure  $\text{FeCl}_3$ . The gas, however, still contains some  $\text{FeCl}_3$ .
- c) The separation is carried out in two stages. In the first stage the gas mixture is chilled to an intermediate temperature at which dissociation of  $\text{FeCl}_3$  to  $\text{FeCl}_2$  does not take place. The gas is then cooled further to  $60-70^\circ\text{C}$  above the dew point of  $\text{TiCl}_4$ . Most of the  $\text{FeCl}_3$  separates as an almost completely dry solid. The advantage is that no liquid  $\text{TiCl}_4$  is required.

Further purification of  $\text{TiCl}_4$  is carried out by the methods described previously.

An important step in this process is roasting of  $\text{FeCl}_3$  in the presence of oxygen to recover  $\text{Fe}_2\text{O}_3$  and chlorine gas. This is carried out in a fluidized bed reactor at  $700-950^\circ\text{C}$  [29,30].

A raw materials cost analysis [28] suggests that direct chlorination of ilmenite offers a distinct economic advantage over chlorination of natural and synthetic rutile, or  $\text{TiO}_2$ -rich slags, since ilmenite feedstock is far less expensive. However, until a commercial plant for direct

chlorination of ilmenite is constructed and operated, meaningful comparisons cannot be made.

#### 5.2.4 Other Chlorination Methods

Other methods for chlorination such as use of alternative chlorinating agents (HCl gas), electrolysis of chloride baths using a TiC anode, have been proposed, but have not been developed beyond the laboratory stage. Most of these methods are of no commercial interest. One method [31], however, appears to hold some promise in which ilmenite is dissolved in  $H_2SO_4$  and then reacted with KCl after separation of the iron oxides. The resulting  $K_2TiCl_6$  can be thermally decomposed to  $TiCl_4$  and KCl which can be recycled.

#### 6. Production of Titanium Sponge

The key step in the production of titanium metal is the reduction of titanium tetrachloride. The bulk of the world's production comes from the magnesium (Kroll) or the sodium (Hunter) reduction process. Current world capacity of titanium sponge plants is shown in Table 11.

Both these reduction processes have the principal disadvantage that, as usually operated, they are batch processes and are not, therefore, ideally suited to really large-scale operations. In addition, the processes are extremely capital and energy intensive, and require complex operations. Intensive worldwide research has led to important improvements in the last ten years in the operations of thermal reduction processes [14]:

- increased reactor size with batch sizes of 3000 - 6000 kg sponge;
- helium-sweep method for removing unreacted Mg and  $MgCl_2$ ;
- magnesium recovery cells;
- continuous production of  $TiCl_2$

To date, however, a continuous reduction process has not been reported.

Table 11. Capacities of World Titanium Sponge Plants (tonnes) [3,32]

Country	Process	Capacity 1980	Announced Expansion
<u>United States</u>			
TIMET	Mg	12700	14515
RMI Co.	Na	7710	7710
OREMET	Mg	2040	4500
D-H Co.	Electrolytic	-	1815
	Total	22450	
<u>United Kingdom</u>			
ICI	Na	1815	To be abandoned in 1982
RR Consortium	Na	-	6000 (1982)
<u>Australia</u>			
Western Mining	Mg	-	5000-7500
<u>Japan</u>			
Osaka	Mg	7712*	11000
Toho	Mg	5897	8845
Nippon Soda	Na	1360	2172
	Total	14969	
<u>USSR</u>			
Zaporozhi'y	Mg	5000	
Berezhiki	Mg	5000	
USK Kamenogorsk	Mg	25000	
	Total	35000**	43750
<u>People's Republic of China</u>	Mg	1815**	

\*Includes an estimated 1360 tonnes from Na reduction

\*\*Gross estimate

Several other reduction methods have been studied on laboratory and semi-production scale. The one that is expected to have the nearest term commercial impact is fused salt electrolysis of  $TiCl_4$ . In fact, the D-H Company (Dow Chemical and Howmet) has announced the operation of the first commercial-scale electrolysis plant for producing 1815 tonnes of titanium sponge per year [33].

The problems associated with the production of titanium sponge are also reflected in the high price of metal, a major obstacle to more widespread use of titanium. Although titanium occurs extensively in nature, the cost of producing it from the expensive rutile ore is high. Ilmenite ore is a cheaper and more abundant source of the metal, and it is being increasingly used to manufacture  $TiCl_4$ , the starting material for production of titanium sponge. None of the currently used processes that convert ilmenite, however, is entirely satisfactory and there is scope for further improvement at each stage of the process, as well as for the development of an entirely new reduction method.

New titanium sponge manufacturing plants are being considered in various countries. Since process selection will ultimately determine commercial viability of a new venture for which depreciation costs are very high, various factors need to be carefully considered in making a decision [3,14]:

- a) Capital Investment is among the highest for a titanium sponge plant, compared with other metal producing operations. Table 12 compares these costs for production of a number of common metals. Note that the cost figure for titanium does not include tetrachloride or sodium recycle which may lower costs.



- b) Energy Requirements for producing various metals, including titanium, are shown in Table 13. Titanium requires more energy to produce than any of the other metals and there is considerable scope for reducing the amount of energy required to produce titanium. Electrolytic reduction of titanium chloride too consumes more energy than either aluminium or magnesium, as Table 14 shows. The data suggest that here too considerable energy savings can be achieved. In general, electrolytic reduction of titanium chloride requires less energy than the thermal reduction processes, up to 40% less by one estimate [33]. The process efficiency of the thermal reduction method is only 4% of the theoretical 16 million BTU/tonne [34], so substantial improvement can be made.
- c) Product Quality is probably not as crucial since all three reduction processes produce high-quality sponge. But no matter which process is selected, careful quality control will be required to produce acceptable titanium sponge.

Table 12. Capital Investment for Production of Various Metals

Metal	Cost per Annual Short Ton, 1980 U.S. Dollars
Copper*	7,000
Magnesium	3,000
Nickel	18,000
Chromium	14,000
Aluminum**	4,500
Titanium-Sodium†	9,000-16,000

\*Mining through refinery  
\*\*Includes power facilities  
†Does not include tetrachloride or sodium recycle

Table 13. Energy Required for Production of Primary Metals [35]

Material	$10^6$ Btu/st	kWh/kg*
Titanium magnesium sponge	423	44.23
Titanium sponge sodium	370	32.48
Aluminum	244	25.51
Magnesium	358	36.98
Sodium	92	9.68
Nickel	144	14.96
Copper	112	11.86

\*Does not compensate for fossil fuel efficiency and transmission losses.

Table 14. Calculated Energy Consumption for the Electrolytic Reduction of Selected Chlorides [3]

Chloride	EMF	Electrotechnical Equiv. Amp - hr/kg	Energy Required kWh/kg
$AlCl_1$	1.4	614.76	0.86
$MgCl_2$	2.21	454.50	1.00
$TiCl_1$	2.25	461.52	1.04

(x = 2 to 4)

#### 6.1. Reduction of $TiCl_4$ by Mg (Kroll Process)

The Kroll process, in commercial use since 1946, is at present the predominant method for the manufacture of titanium sponge. Since the current industrial operation differs very little from Kroll's original process, it has a number of technical problems, first noted by Kroll in 1955 [36], which have still not been completely solved.

The process consists of reacting  $\text{TiCl}_4$  with liquid Mg at 850 - 920°C in a sealed steel vessel in an inert gas environment. The reaction products are excess Mg,  $\text{MgCl}_2$ , and titanium sponge. The operating temperature is carefully controlled to maintain liquid  $\text{MgCl}_2$  (m.pt.  $\sim 711^\circ\text{C}$ ) and to prevent a reaction between titanium and the reaction vessel (lowest eutectic in the Fe - Ti system forms at 1085°C [37]). This is accomplished by adjusting the rate of flow of  $\text{TiCl}_4$  since the reaction between Mg and  $\text{TiCl}_4$  is exothermic and no external heat input is required once the reaction has started.

Titanium metal is deposited at the walls of the reaction vessel and as the reaction proceeds, it grows across the crucible to form a complete bridge. It is lanced and the reaction process restarted. Liquid  $\text{MgCl}_2$ , which collects at the bottom, is periodically withdrawn, until the reaction vessel is nearly completely filled with titanium sponge at the end. To prevent the formation of lower chlorides of titanium, up to 15% excess magnesium is used. The magnesium used must be of very high purity, since the purity of the titanium product can only be as high as the starting materials.

The properties of the sponge are governed by the rate of  $\text{TiCl}_4$  feed and by the contact time between  $\text{MgCl}_2$  and the sponge [38,39]. A more rapid feed rate yields finer crystals with high impurities. Carbon, oxygen, and nitrogen are the main impurities which affect product quality. The sources of carbon contamination are  $\text{TiCl}_4$  from the vacuum system.  $\text{TiCl}_4$  is also the source for oxygen and nitrogen contamination. To minimize the impurity levels in the sponge, the reaction vessels are now lined with titanium liners [40]. Also, the  $\text{TiCl}_4$  is purged with argon after its distillation.

#### 6.1.1. Separation of Titanium from the Reaction Products

Various methods are used to separate the titanium sponge from excess

magnesium and magnesium chloride in the reaction product. In the acid leaching process, the reacted mass is treated with dilute HCl containing an inhibitor to dissolve Mg and  $MgCl_2$ . Since the dissolution of  $MgCl_2$  is exothermic, the heat evolved raises the temperature of the reaction product and surface contamination of titanium may take place. Leaching is, therefore, carried out below 25°C. Dissolution of Mg, on the other hand, liberates hydrogen which dissolves in titanium even at room temperature. It can be removed by vacuum heat treatment, but that only adds to the costs of production. Generally, the sponge titanium must be leached two or three times with intermediate grinding of the sponge to ensure complete removal of all magnesium products.

The problem of hydrogen contamination can be avoided by leaching in a mixture of hot, dilute acids (8% HCl, 3%  $HNO_3$ ). In this TIMET method leaching is carried out in rotary drums made of titanium (20 m long, approx. 2.5 m dia.).

The leaching method is now being replaced by vacuum distillation, utilizing either top or bottom condensers [41]. An example of a vacuum distillation apparatus is given in [42]. To facilitate the removal of the reaction mass after distillation, the reaction chamber is fitted with a thin steel liner. Careful operation around 875 - 920°C at a vacuum of 0.1 torr will remove most of the magnesium and magnesium chloride which condense at the bottom of the apparatus. The distillation process takes about 26-36 hours for a 1500 kg batch size, but it may take as long as 90 hours [43]. Raising the temperature and lowering the vacuum have not improved the results [44].

An alternative method is to distill off Mg and  $MgCl_2$  in a flowing inert gas environment. This is the OREMET helium sweep method [91] in which the magnesium products are swept out by helium and they then condense in the cooler regions of the gas stream. The principal advantages are lower equipment and

operations costs.

Compared with acid leaching, vacuum distillation for the separation of titanium sponge from the magnesium products has definite advantages. Excess magnesium is recovered as the metal and can be directly recycled.  $MgCl_2$  is recovered as a pure dry solid and can be used without further purification in magnesium electrolysis cells. No hydrogen contamination of the titanium sponge takes place, and yields are, in general, higher. On the other hand, capital and labor costs are higher for the vacuum distillation method and it is a batchwise operation.

Table 15 compares the impurity levels in titanium sponge after acid leaching and vacuum distillation. Both methods now yield metal with 80 - 90 BHN.

Table 15. Typical Analyses of Titanium Sponge after Acid Leaching and Vacuum Distillation [21]

Element	Acid Leaching %	Vacuum Distillation %
Titanium	> 99.0	> 99.3
Iron	0.25	0.30
Magnesium	0.3 - 0.5	0.10
Nitrogen	0.03	0.03
Carbon	0.07	0.05
Chlorine	0.15	0.15
Oxygen	< 0.20	< 0.10

Iron is a major impurity in the sponge [45,46], picked up by  $TiCl_4$  and the reaction products from the steel reaction vessel and other components.

Recently, however, RMI Co. has begun to market a high-purity metal with < 0.05% Fe. This metal is reported to have superior corrosion resistance [47].

#### 6.1.2. Variations of the Kroll Process

A variation of the basic Kroll process has been proposed by Levy et al. [48] in which magnesium is replaced by a calcium-magnesium eutectic (82% Mg - 18% Ca). The alloy reacts very rapidly with  $TiCl_4$  and the reaction quickly goes to completion. This method yields a very pure product and may be amenable to continuous operation.

In another variation two-stage reduction has been suggested [49].  $TiCl_4$  is first reduced to  $TiCl_2$  with sodium, followed by reaction of liquid magnesium with a mixture of liquid  $TiCl_2$  -  $TiCl_3$  in NaCl. This method yields high-quality metal.

A completely new approach has been described by the Halomet Co. [50]. In this method  $TiCl_4$  is reacted with liquid magnesium in a double-walled vessel to give molten titanium at 1727°C and  $10^3$  torr. This sinks to the bottom of the vessel lined with  $MgAl_2O_4$ . Water cooling of the inner wall helps to form a solid  $MgCl_2$  layer which prevents chemical attack and also provides insulation. Titanium can be withdrawn from the bottom and  $MgCl_2$  from above the molten titanium. The process may be operated on a continuous basis. Titanium alloys can also be prepared by introducing halides of constituent metals in stoichiometric proportions.

#### 6.1.3. Cost Estimates of the Kroll Process

A recent report [51] estimates investment costs of \$9,000 - \$13,000 per annual tonne of titanium sponge. The Kroll process, as noted previously, is very energy-intensive, requiring approximately 44 kWh/kg of metal.

Electrolysis of magnesium chloride requires the most energy in the Kroll process. Japanese and U.S.S.R. producers have developed electrolysis cells with capacities of 100,000 - 150,000 amp, with an average consumption of only 13.5 kWh/kg, while U.S. producers require 16-18 kWh/kg of magnesium [51a]. Vacuum distillation is the second largest energy consumption step in the Kroll process. Japanese producers are conducting vacuum distillation without any cooling after reduction of  $TiCl_4$  with magnesium. This step is reported to save between 800 and 1000 kWh per tonne of titanium sponge.

To put the total process into perspective, Fig. 14 [52] shows the material flow and energy requirements for each individual step in the production of 1 tonne of titanium metal from ilmenite by the magnesium reduction of the tetrachloride.

#### 6.2. Reduction of $TiCl_4$ by Na (Hunter Process)

The reduction of  $TiCl_4$  by sodium is a twin to the magnesium reduction process. Since Hunter's first successful attempt in 1910 [53], the sodium reduction process has evolved in a number of variations:

i) In the DEGUSSA\* process [54] a mixture of NaCl and KCl is covered by a layer of metallic sodium and heated to 700 - 800°C in an iron crucible. The reaction is started by passing in  $TiCl_4$  vapor. Since the reaction between sodium and  $TiCl_4$  is much more exothermic than the reaction with magnesium, process control is more difficult. The temperature must be carefully controlled in a narrow range between 800 and 870°C, since NaCl freezes below 800°C and sodium boils at 877°C. The liquid NaCl can be withdrawn during the reaction, making continuous operation possible.

ii) A major improvement has been the introduction of a two-stage process [55,56]. In the first stage  $TiCl_4$  is reduced to  $TiCl_2$  at 235°C

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\* Deutsche Gold-und Silberscheidanstalt, West Germany

by liquid sodium. The reaction is carried out in a reactor with continuous stirring. The flow of sodium is stopped when all the  $TiCl_4$  has been reduced to  $TiCl_2$ . In the second state the melt containing  $NaCl \cdot TiCl_2$  is reacted with additional sodium at 800 - 850°C under argon. The liquid  $NaCl$  is continuously removed. The reaction takes about 8 hours, after which the temperature is raised to 930°C for a short time to convert any unreacted material. Since a large amount of heat is dissipated in the first stage, closer temperature control is possible in the second stage. This makes it possible to control the rate of titanium deposition and large crystals can be obtained. Titanium is separated from the reaction product by leaching in dilute  $HCl$ . A schematic flowsheet of the process is shown in Fig. 15.

iii) ICI\* [57] has developed another variation of the basic Hunter process. In this method finely powdered sodium chloride is partially filled in a steel reaction vessel and heated to a temperature between 200 - 600°C. Liquid sodium is slowly fed in from the top and  $TiCl_4$  vapor is blown in from the bottom of the reactor. The sodium chloride is constantly levitated to facilitate contact between the reactants. The flow of sodium and  $TiCl_4$  is shut off when the reactor is completely filled. The metal produced in this method is in a finely powdered form and is consolidated by heating the reacted product to 800°C for about 2 hours. It is then leached to separate the sodium products.

In 1980, ICI produced 1815 tonnes of titanium sponge by the sodium reduction process. This plant will, however, be abandoned in 1982 and is to be replaced by a new 6000 tonne facility to begin operation in the

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\* Imperial Chemical Industries, U.K.



the same year [32].

iv) A low temperature variation of the two-stage sodium reduction process has been developed by Homme and Wong [58] in which liquid sodium is reacted with solid  $\text{TiCl}_2 - \text{NaCl}$  in the second stage. Titanium metal with an average hardness of 76 BHN has been obtained.

#### 6.2.1. Cost Estimates of the Hunter Process

No information is available about investment and operational costs of the Hunter process. Since the unit costs of producing sodium are lower than magnesium, the Hunter process will probably be more economical than the Kroll process. However, the Hunter process is competitive only if a source of particularly cheap sodium is available.

#### 6.3. Comparison of Magnesium and Sodium Reduction Processes

To obtain a better perspective on the thermal reduction of titanium tetrachloride to the metal, a comparison of the magnesium and sodium reduction methods is useful.

The Kroll process has higher plant costs than the Hunter process because of the need for a vacuum distillation unit for separation of magnesium and magnesium chloride from the titanium sponge. An excess ( $\sim 15\%$ ) of magnesium must be used for reduction, while reduction with sodium can be carried out using nearly stoichiometric amounts. In addition, both liquid sodium and titanium tetrachloride can be fed at controlled rates in the Hunter process, making it easier to control the operating conditions. The latter is critical to the sodium reduction reaction which must be carried out in the narrow temperature range,  $800 - 870^\circ\text{C}$ . On the other hand, the sodium reaction products require relatively simple handling techniques, since liquid sodium can be purified by filtration and sodium chloride is non-hygroscopic. But there are definite disadvantages in the Hunter process.

Since the boiling point of sodium chloride is very high (1413°C), vacuum distillation to separate it from titanium sponge is unattractive. Leaching must, therefore, be carried out. The dissolved sodium chloride is recovered by evaporation, an extremely energy intensive operation. Finally, a choice between the Kroll and the Hunter processer can only be made if there is a source of cheap sodium metal available.

Currently, there are a total of 7 plants in the Western world for production of titanium sponge using the magnesium or sodium reduction process (see Table 11). The Soviet Union has three magnesium reduction plants with a total estimated capacity of 42,000 tonnes per year, while China produces an estimated 1800 tonnes of titanium sponge per year by the Kroll process.

#### 6.4. Other Reduction Methods

Several other methods have been studied to convert various titanium compounds to metallic titanium. However, none of these methods has achieved any commercial success.

##### 6.4.1. Amalgam Reduction

One of the first suggestions, made by the Kennecott Copper Corporation [59], was to reduce  $TiCl_4$  with sodium amalgam instead of pure sodium. The process was designed for continuous operation of low temperatures. However, insurmountable problems with separation of mercury and sodium chloride from the titanium sponge were encountered and further development was discontinued.

A later suggestion [60] was to use a sodium-calcium mixed amalgam instead of sodium amalgam. This forms a low melting  $NaCl - CaCl_2$  eutectic (m. pt.  $\sim 450^\circ C$ ) and a fluid amalgam (fine suspension of  $TiHg$  particles in Hg [61]).

These products can be easily separated in an apparatus shown in Fig. 16 [62] and the mercury distilled off. This method gives very high purity metal, but the distillation of mercury requires very large amounts of energy.

In another variation [62] the reaction products, from the reduction of  $TiCl_4$  with sodium amalgam at 250 - 300°C, were separated by dissolving NaCl in suitable aqueous solutions. The dilute Ti amalgam is concentrated by filtration and the mercury distilled off. The product is a metal with a BHN hardness of 120. This method is amenable to continuous reduction of  $TiCl_4$ , but the problems associated with the handling of large quantities of mercury make it commercially unattractive, although a pilot-plant scale operation has been successfully carried out (Fig. 17) [62].

Attempts to reduce  $TiCl_4$  with Na-Zn amalgams have been largely unsuccessful since the activity of sodium in zinc is very low.

#### 6.4.2. Reduction of Other Titanium Halides

High-purity titanium metal can be prepared by the van Arkel-de Boer process in which titanium tetraiodide is thermally dissociated on a hot tungsten filament. However, the high costs involved make this method commercially unattractive for either primary metal production or as a secondary refining process.

Attempts have also been made to reduce non-hygroscopic  $TiF_4$  with silicon. The  $TiF_4$  is produced by reacting  $TiO_2$  with HF. This method yields a product with a high silicon content. Similarly, the reduction of lower halides ( $TiCl_2$ ,  $TiBr_2$ ) has been largely unsuccessful.

#### 6.4.3. Direct Reduction of $TiO_2$

Theoretically,  $TiO_2$  can be reduced directly with calcium or calcium

hydride ( $\text{CaH}_2$ ). In practice, however, the reduction yields a metal contaminated with oxygen. At  $1000^\circ\text{C}$ , the metal in contact with calcium will contain about 0.07 wt% oxygen [63].

#### 6.4.4. Plasma Reduction

In a method proposed by McLaughlin [64]  $\text{TiO}_2$  powder can be reduced to titanium metal by a hydrogen plasma in the temperature range  $1952 - 2902^\circ\text{C}$ . The liquid titanium is recovered as finely divided droplets. A product with  $> 99.8\%$  titanium has been obtained.

Plasma reduction of  $\text{TiCl}_4$  using a hydrogen plasma has also been suggested [65,66]. The reaction occurs at very high temperatures in the presence of an arc which generates the plasma. The principal disadvantage in these methods is hydrogen contamination of the metal, making vacuum degassing necessary.

#### 6.4.5. Carbothermic Reduction

Carbon will reduce  $\text{TiO}_2$  to the metal at very high temperatures and reduced pressures, but the metal invariably contains considerable amounts of carbon and oxygen.

Extensive research [67] has been carried out to reduce  $\text{TiO}_2$  with carbon or titanium carbide in a carbothermic process similar to that used for the production of vanadium or niobium. Graphite- $\text{TiO}_2$  and  $\text{TiC-TiO}_2$  powders were compacted and the reduction was carried out by direct heating in very high vacuum. Titanium dissolves appreciable amounts of oxygen and carbon [37] which are very tightly bound in the lattice. Thus, removal of carbon and oxygen is extremely difficult. As Fig. 18 [67] shows, in order to obtain high-purity titanium metal by carbothermic reduction, the process must be carried out near the melting point of titanium ( $1770^\circ\text{C}$ ) and a vacuum  $> 10^{-9}$  atm

( $\sim 10^{-6}$  torr). The experiments with  $\text{TiO}_2$ -graphite and  $\text{TiO}_2$ -TiC yielded a metal with very high oxygen and carbon contents. No improvement was achieved even by carrying out the reduction above the melting point. On the other hand, carbothermic reduction was successfully applied to produce a high-purity Ti-Mo alloy with high Mo contents ( $> 50\%$ ), since the thermodynamic equilibrium conditions are much more favorable (Fig. 19). This method can potentially be used to produce master alloys [67].

### 6.5. Electrolytic Reduction Processes

Molten salt electrolysis for the production of titanium is the process that is expected to have the nearest term commercial impact on titanium sponge production.

Development work on the electrolytic process has been carried out for nearly three decades, but now the D-H Company has announced the operation of a plant with an annual capacity of 1815 tonnes sponge per year [33]. Successful tests with a prototype electrolytic cell have also been carried out by Sony Research Corporation in Japan [68].

The production of titanium by electrolysis of aqueous solutions is unlikely to be successful [7] since all titanium compounds are readily hydrolyzed.

#### 6.5.1. Electrolysis of Molten Oxide Baths

The deposition of titanium from oxide baths has been tried, but the results have generally been unsatisfactory. The principal difficulty is that  $\text{TiO}_2$  is only slightly soluble in most common low-melting substances. It does dissolve in alkali borates and phosphates, and in NaF and KF, and in  $\text{K}_2\text{TiF}_6$  [46], but these solutions melt between 700 and 900°C. In general, the metal deposits from these baths are highly porous and contain considerable amounts of oxygen.

Attempts have been made to deposit the titanium from these baths on molten metal cathodes (Cd, Zn, Pb) from which the titanium can be recovered by distillation. The main problem here is that the melting point of the liquid metal cathode increases rapidly with increasing titanium content. By controlling the amount of titanium deposited, however, cell efficiency decreases.

#### 6.5.2. Electrolysis of Molten Chlorides

By contrast, electrolysis of molten chlorides yields high-quality titanium deposits [68, 69], but there are some outstanding problems:

- i)  $TiCl_4$  is in general insoluble in alkali and alkaline earth salts. It must, therefore, be reduced to the more soluble  $TiCl_2$ . High concentrations of  $TiCl_2$  in the electrolyte, however, lead to poor quality deposits [69, 70].
- ii) The high concentration of  $TiCl_2$  in the bath leads to low current densities, since ion transport causes the  $TiCl_2$  to reoxidize to  $TiCl_4$  at the anode. This makes it necessary to separate the anolyte and catholyte sections of the cells by means of a diaphragm, which, however, increases the cell voltage.
- iii) High-purity titanium can only be deposited from very pure oxygen-free electrolytes. Electrolysis, must, therefore, be carried out in an inert gas atmosphere, and air and water vapor ingress must be prevented.
- iv) Oxygen-free electrolytes cause "anode effects" at the graphite anode (well-known from aluminum electrolysis [70a]) which adversely affect the electrolysis.
- v) Titanium deposits on the cathode as dendritic aggregates. Unless

the cell conditions are carefully controlled, particularly the average titanium valence, the metal deposits as a powder with poor adhesivity, and tends to flake off, resulting in lower yields. Moreover, the cathode deposit must be leached to remove the residual electrolyte.

Excellent results have been achieved [69, 71] by electrolysis of  $\text{KCl} - \text{LiCl} - \text{TiCl}_2$  and  $\text{KCl} - \text{LiCl} - \text{NaCl} - \text{TiCl}_2$  (melting points of the alkali chloride eutectics are  $347^\circ\text{C}$  and  $362^\circ\text{C}$ , respectively) in large diaphragm-type electrolytic cells (72 in. diameter). The cells were operated at  $650 - 800^\circ\text{C}$  with continuous feeds of  $\text{TiCl}_4$  to the molten chloride mixture. Titanium was deposited at the cathode from  $\text{TiCl}_2$ , formed by reduction of the tetrachloride. The product is titanium metal with an average hardness of 100 - 150 BHN.

More recent Japanese work [68] with a  $\text{BaCl}_2 - \text{MgCl}_2 - \text{CaCl}_2 - \text{KCl} - \text{NaCl} - \text{TiCl}_2 - \text{TiCl}_3$  electrolyte at  $500 - 560^\circ\text{C}$ , gave a high-quality titanium deposit ( $\sim 100$  BHN). Electrolysis was carried out in a large prototype cell (internal capacity  $\approx 40$  gals) using a rotating stainless steel cathode and a carbon anode (Fig. 20). The fused salt mixture is circulated through the three parts of the cell: the high-temperature section, where the salts are melted; the cooler section, where controlled precipitation of crystallites occurs; and the electrolysis section. The cathode is leached in dilute  $\text{HCl}$  to remove any adhering electrolyte, and the titanium deposit is stripped from the cathode.

The D-H Company electrolytic process [33] employs a  $\text{KCl} - \text{LiCl} - \text{TiCl}_2$  electrolyte at  $520^\circ\text{C}$  to deposit titanium on a circular steel cathode.

Table 16. Typical Analyses of D-H Company Electrolytic Titanium  
Compared with Kroll and Hunter Process Titanium (percent)

Element	D-H Electr. Process	Kroll Process -Vac. Dist.	Kroll Process -Leaching	Hunter Process
Oxygen	0.035-0.065	0.10	0.10	0.10
Nitrogen	0.002-0.003	0.015	0.015	0.015
Carbon	0.009-0.011	0.020	0.025	0.020
Iron	0.010-0.020	0.120	0.15	0.05
Hydrogen	0.003-0.005	0.010	0.03	0.05
Chlorine	0.010-0.035	0.120	0.20	0.20
BHN	60-90	-	-	-

Table 17. Data for the D-H Company Commercial Titanium Sponge Plant

No. of Multiple Anode Cells	70	Titanium Current Efficiency	80%
Pot Line Current	22,500 amps	Average Cell Voltage	6.2V
Operating Factor	95%	DC kWh/kg of metal	17.4
Titanium Yield Efficiency	98%	Electrolyte:	KCl+45-60% LiCl

Details of the electrolytic cell are given in [33], and the electrochemical reactions are shown schematically in Fig. 21. The deposits are removed when a cathode has received about 20,000 amp. hours. Any adhering salt is removed by a 0.5% HCl solution in a countercurrent leacher. The process flowsheet is shown in Fig. 22. High quality metal (Table 16) has been



produced on a continuous basis in a prototype cell. A demonstration plant of 450 tonne capacity is scheduled to go into operation in 1981 and a 1815 tonne commercial plant is expected to start up in 1984. Table 17 presents some key figures for the 1815 tonne commercial plant.

### 6.5.3. Electrorefining

Electrorefining of impure titanium is becoming increasingly important, not only for purification of the metal, but also for recycling titanium alloy scrap.

#### 6.5.3.1 Impure Titanium Metal

Major efforts [72] have been made to recover titanium from metal contaminated with oxygen, carbon, and nitrogen. Electrolysis in an 85 : 15 NaCl -  $K_2TiF_6$  bath at 750 - 850°C gave yields of 91% titanium from TiC and 62% from Ti(C,O,N). The crude metal was then electrorefined using a NaCl -  $TiCl_2$  or LiCl - KCl -  $TiCl_2$ , electrolyte to yield a product with an average hardness of 73 - 95 BHN.

#### 6.5.3.2. Titanium Alloys

Electrolytic refining of titanium alloys is more complex. Control of the rate of deposition of the alloying elements is the major problem. Russian work [73] has shown that alloy powders can be prepared by controlled electrolysis.

#### 6.5.3.3. Titanium Scrap

Most of the titanium scrap is contaminated with oxygen and it can be refined by the methods used for impure metal (see 6.5.3.1.). Or it can be chlorinated to  $TiCl_4$  and pure metal is then electrodeposited. On the other hand, the scrap can be reacted with  $TiCl_4$  to yield the lower chlorides which can then be electrolyzed [74, 75].

## 7. Consolidation of the Titanium Sponge

The titanium sponge obtained from the reduction cycle must eventually be consolidated to ingots for mill shape fabrication. Most refractory crucible materials react violently with molten titanium. Thus, conventional melting techniques cannot be used for titanium and other methods must be employed.

One such method is the consumable-electrode vacuum-arc melting technique used to consolidate sponge, scrap, and alloy additions. The use of high vacuum has the added advantage of removing much of the hydrogen and other low boiling impurities [76].

The non-consumable electrode melting technique is used in two modern variations of the basic electric arc melting technique. In the "DURARC" process, as illustrated in Fig. 23, a water-cooled copper electrode tip with built-in field coils is used to keep the arc moving around the electrode tip. The intense heat generated is distributed uniformly over the tip surface and it ensures a uniform temperature in the melt [77]. In the "ROTARODE" method [78] the melting furnace has an inclined water-cooled copper electrode (Fig. 24) which is rotated at high speed (100-200 rpm). These techniques reduce the capital investment in pressing equipment used to produce electrodes for the consumable-arc technique. Also, the energy required for melting is less for the non-consumable electrode technique because of reduced heat losses. In general, the metal is remelted two or more times to obtain a homogeneous ingot. Large ingots from 35-40 in. in diameter and weighing up to 10 tonnes\* are now being produced, in increasing proportions from revert scrap. In 1980 35-40%

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\*Leybold-Heraeus, West Germany reportedly has a consumable electrode melting furnace designed to produce ingots weighing up to 30 tonnes [79].

of titanium ingot charge was revert scrap, and in some cases, 100% scrap ingots have been produced [3].

A recent development in melting of titanium sponge is plasma electron beam melting. The charge is melted by two plasma guns. In Japan this technique has been used on production basis to produce cast slabs weighing up to 3.5 tonnes (maximum dimensions: 10 x 45 x 100 in.) [80].

Table 18 lists the principal producers of titanium metal ingots in the Western World.

Table 18. Titanium Ingot Capacity of the Main Producers in the Western World (tonnes/yr)

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<u>U.S.A.</u>	TMCA (15000); RMI (8000); Oremet (5000); Howmet (3000); Crucible Steel (3000); Teledyne Allvac (1500); Lawrence Aviation; Martin Marietta Aluminum
<u>Japan</u>	Kobe Steel (3000); Nippon Mining (1500); Furukawa Electric (500); Nippon Stainless (500)
Other plants in the U.K. (I.C.I.); Sweden (Sandvik); France (Pechiney); Canada (Atlas Steel and Ionarc Smelters); West Germany (Krupp and Contimet).	

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## 8. Properties of Titanium and its Alloys

Titanium is a silvery white metal with a density of  $4.51 \text{ g/cm}^3$ . It also has high-strength to about  $800^\circ\text{C}$ . This high strength to weight ratio makes titanium very attractive for a variety of structural

applications. In addition, titanium also has excellent corrosion resistance because the metal forms a compact, tightly-adhering oxide scale on the surface. The metal is resistant to dilute acids and alkalis, and most chloride solutions. At room temperature it is attacked only by HF, and it is also not resistant to boiling acids. Titanium is also generally not susceptible to stress corrosion cracking, although it is known to crack in certain environments [81].

At temperatures below 300°C, titanium only slowly reacts with air, ammonia, hydrogen, steam, and hydrocarbons. The reaction is fairly rapid at higher temperatures (titanium is the only metal that burns in nitrogen). This is particularly serious for titanium, since the gaseous elements not only form surface compounds, but also dissolve in the underlying metal, thus causing severe embrittlement. Furthermore, with the exception of hydrogen, the impurities (O,N,C) cannot be removed by vacuum heat treatment. Thus, all hot working operations with titanium must be performed in high vacuum or an inert environment. However, if the surface is contaminated during forming operations (high speed machining, cold rolling), it can be decontaminated by vacuum annealing at 900°C to dissolve the surface oxide in the bulk. Interestingly enough, oxygen which was originally considered to be a detrimental impurity, is now a very useful alloying element when present in small amounts. It raises the tensile and fatigue properties at moderately high temperatures without significant loss of ductility or fracture toughness. The effect of various impurities on the mechanical properties of titanium are shown in Fig. 25a and 25b [46].

Titanium exists in two allotropic modifications, low-temperature

hexagonal  $\alpha$ -titanium ( $c/a = 1.587$ ) and body-centered high temperature  $\beta$ -titanium. The  $\alpha/\beta$  transformation temperature is  $883^\circ\text{C}$ , but the presence of an alloying element can alter both the transformation temperature and the kinetics (the  $\beta$ -structure cannot be retained by quenching pure titanium from the  $\beta$  region). Alloying, in fact, is used to stabilize certain crystal structures to improve the properties of unalloyed titanium, as Table 19 clearly shows for various commercial titanium alloys.

Depending on the alloying additions and the subsequent heat treatment, alpha, near-alpha, alpha + beta, and beta titanium alloys can be obtained. The alpha stabilizing elements are Al, Zr, Sn, and O, while the beta stabilizers are V, Mo, Fe, Cr, W. The properties of the alloys are accordingly determined by these alloying additions:

- single phase alpha alloys are solid solution strengthened. They exhibit low to medium strength ( $\sim 90 \text{ kp/mm}^2$ ), are easily welded, and have good stability to  $550^\circ\text{C}$ .
- near alpha alloys,  $\alpha + (\beta)$ , have 1-2 wt. % of a beta stabilizer to improve the strength and hot workability of the alpha alloys.
- alpha + beta alloys have 4-6% of a beta stabilizing element and can be strengthened by martensitic transformation and precipitation of the  $\beta$ -phase. The alloys have good creep strength to  $450^\circ\text{C}$ .
- beta alloys contain large amounts of beta stabilizers. Heat treatment produces a stable beta structure and strengths well over  $130 \text{ kp/mm}^2$  can be achieved. Decomposition of the beta phase, however, results in omega phase formation which is coherent with the beta matrix. Omega embrittles the beta phase, so that its formation must be prevented.

Table 19. Typical Composition and Properties of Commercial Titanium Alloys [46]

Type	Composition %	Ult. Tensile Strength kp/mm <sup>2</sup>		Elongation (annealed) %	BHN
		annealed	hardened		
α	> 99.9 Ti (unalloyed)	30-70	-	18-30	130-200
	5Al, 2.5Sn	77-88	-	15-18	250
	6Al, 2Sn, 4Zr, 2Mo	91	-	25	-
	5Al, 5Sn, 5Zr	84	-	20	250
	2Cu	63	79	25-30	-
α(+β)	2Al, 1Mo, 2Mn	73	93	22	-
	8Al, 1Mo, 1V	91	-	20	280
	2.25Al, 11Sn, 5Zr, 1Mo, 0.2Si	102	115-118	11-12	-
	8Al, 4Co	115	135	8-18	-
α + β	2Al, 11Sn, 4Mo	107	-	20	-
	6Al, 4V	94-115	100-135	12-15	260
	4Al, 4Mn	97-104	114	16-25	-
	7Al, 4Mo	100-108	128	13-20	260
	6Al, 6V, 2Sn	105	126	20	-
	5Al, 2Cr, 1Fe	104	131	17	-
	5Al, 1.5Cr, 1.5Fe, 1.5 Mo	105	133	17	-
	6Al, 5Zr, 1W, 0.2Si	-	101	-	-
3Al, 6Sn, 5Zr, 2Mo, 0.5Si	-	110	-	-	
β	3Al, 13V, 11Cr	88-95	119-130	14-20	220
	15Mo	70	95	25	-
	11Al, 8V, 5Fe	125	147	8	-

Finally, a new class of alloys, based on Ti<sub>3</sub>Al and TiAl, has been developed. They are, however, very brittle and difficult to form, and have found only limited application.

### 8.1 Mill Shape Fabrication

Titanium mill products such as billet, sheet, strip, bar, and tubing

can be fabricated in conventional equipment used to forge or roll stainless steel and nickel-base alloys [3, 82]. Titanium slab is rolled on mills interspread with stainless steel with only slight modifications to prevent surface contamination. In the TIMET plant in Toronto, Ohio, however, 48 in. wide titanium strip is continuously annealed in a vacuum furnace to yield strip with an uncontaminated surface [3].

Casting of titanium and its alloys presents no major difficulties, although the properties of castings are generally inferior to the forged materials [79, 83].

Most conventional welding methods can be used with titanium, although a protective environment is necessary. Diffusion bonding is exceptionally well-suited for titanium, just as is explosive welding of tubes to the titanium tubesheet in condensers [84].

Titanium powder metallurgy has made significant advances in recent years with the fabrication of complex shapes [85]. The mechanical properties of powder metallurgy products are generally inferior to forgings, although hot isostatic pressing may lead to significant improvements [85].

Table 20 [3] gives the breakdown of titanium mill product shipments.

Table 20. Titanium Mill Product Shipments (percent)

Product	1960	1970	1980
Bar and billet	80	79	62
Sheet, strip, and plate	20	13	20
Tubing and extrusions	negligible	4	14
Other	negligible	4	4

## 9. Uses and Applications of Titanium

The principal use of titanium is in the aircraft gas turbine in modern jet engines with an average titanium content of 20-30%, and fully 40% of all titanium mill products shipped are eventually used in various jet engine parts. This is graphically illustrated in Fig. 26.

The second largest use of titanium is in aircraft structures of commercial and military airplanes. Table 21 shows the relatively high titanium content in different types of aircraft [86].

Although the aerospace applications for titanium appear to have reached maturity, any meaningful displacement of titanium in these applications is unlikely in the near future. New materials such as fiber-reinforced composites could, however, change this. In fact, as Table 21 shows, these materials now make up 5-10% of the structural materials in some airplanes.

Titanium also finds application in construction of various industrial equipment. Table 22 shows the current industrial application of titanium [84]. The chief forms are tubing and pipe, primarily because of extensive condenser tube applications in power plants. The other applications are in dimensionally stable anodes for production of chlorine and sodium chlorate, chemical process equipment (e.g. pulp and paper manufacturing), and automotive, marine, and steam turbines. Seawater desalination plants also employ titanium as construction material. A novel application is in medical prosthetic devices such as hip joints, or in the cases for heart pacers.

The growth in industrial applications has been rather dramatic [3, 87]. In 1968, less than 900 tonnes of titanium was used in various industrial processes. Since then the market has grown at annual rate of



17% and in 1979, 5400 tonnes, or 30% of the titanium mill products, were used outside the aerospace industry.

Table 21. Approximate Contents of Structural Materials in Various Aircraft [86]

Material	Military Aircraft			Commercial Aircraft
	B1	Tornado	F16	Airbus A300
	(U.S.)	(U.K.)	(U.S.)	(Europe)
Aluminum	41%	70%	57%	75%
Titanium	21%	19%	9%	6%
Steel	7%	7%	14%	7%
Fiber Reinforced Composites	-	-	10%	5%
Others*	31%	3%	20%	7%

\*Not including fiber-reinforced composites

Table 22. Free World Industrial Utilization of Titanium in 1979

Mill Products	Tonnes	Application	Tonnes
Tube, Pipe	4990	Heat Exchangers	4990
Sheet, Strip	1814	Electrodes	2268
Plate	1360	Tanks and Piping	1814
Bar, Billet	908	Miscellaneous	<u>454</u>
Wire	227		9526
Castings	<u>227</u>		
	9526		

For most chemical applications titanium is used in the unalloyed form. But for most other applications titanium alloys are employed. Table 19 lists the most important commercial alloys of the one hundred or so alloys of titanium that have been developed in the past three decades [84]. In the U.S., however, only relatively few alloys are used in production and these are given in Table 23 [84]. Ti-6Al-4V is

Table 23. Utilization of Titanium Alloys in the United States (percent of total shipments)

Composition	1961	1971	1980
Ti-6Al-4V	45	56	52
Unalloyed Ti	16	19	29
Ti-5Al-2.5Sn	15	7	5
Ti-6Al-6V-2Sn	2	7	6
Ti-8Mn	10	2	< 1
Ti-13V-11Cr-3Al	10	1	< 1
Ti-8Al-1Mo-1V	1	3	3
Ti-6Al-2Sn-4Zr-2Mo	-	3	2
Ti-6Al-2Sn-4Zr-6Mo	-	-	1
Other	2	3	< 1

the most extensively utilized titanium alloy, but shipments of unalloyed titanium have also increased significantly.

A recently developed titanium alloy deserves special mention. NITINOL, a so-called "Memory-Alloy" with 55% Ni and 45% Ti [88], has a

remarkable ability to revert to its original shape. For example, if a hot formed NITINOL mill shape is cold-rolled (maximum degree of reduction 8%) to a different shape, the product will revert to its original mill shape simply by heating at 150-200°C. Potential applications of these alloys could be in giant space antennas.

#### 10. Production and Prices

The first commercial mill products were shipped by TIMET Company in 1950. From that time to the present, the overall growth of titanium shipments has been 8% annual [3, 84]. Fig. 27 shows the production of titanium mill products in the U.S. Superimposed on this diagram are wide fluctuations, reflecting variations in the demand for the metal. In the late 1950s the demand dropped 50% as the military strategy shifted from manned aircraft to missiles. In the 1960s commercial jets were being built and demand for titanium was high. Cancellation of the SST program in 1971 caused a slump in demand from 1970 - 1972. Demand surged again from continued buildup of commercial and military aircraft until 1974 when the US and the rest of the world went into a recession. Since then, renewed aerospace orders and expansion of industrial applications have led U.S. production of titanium to a high of 19,500 tonnes in 1979 [84].

In 1979, the U.S.S.R., a major exporter of titanium sponge besides Japan, stopped all exports of sponge. This has led to a major effort to add new sponge manufacturing capacity, particularly in Europe, the main recipient of Russian titanium sponge. New greenfield sponge plants are being considered seriously in France, Australia, Canada, Brazil, and India. Recently, however, the USSR has resumed the export of titanium

sponge [89].

The price of titanium actually declined in current dollars from 1950-70. However, as a result of inflation, the price has increased rapidly since then. Table 24 [90] shows the general price trends of the metal and various raw materials. One reason for the relatively high cost of the metal may be the shortage of refining capacity. With the addition of new production capacity, the titanium price structure will be more in line with other prices.

Table 24. Prices for Titanium Sponge(per pound)and Various Raw Materials (per tonne) in U.S. Dollars

<u>Sponge</u>	1964-72	1974	1976	1978	1980	1981*
Domestic	1.32	2.25	2.70	3.28	7.02	7.65
Japan	1.20-1.25	1.70-1.75	2.45-2.50	3.10-3.30	7.6-8.5	8.85-10.03
U.S.S.R.	2.31	2.31	-	-	-	-
<u>Raw Materials</u>						
Ilmenite	21-26	55	55	50	55	65-70
Rutile	115-193	573-606	562	358-386	468-496	496-524
<u>Slag</u>						
Canada	50	60	60	110	115	135
S. Africa	-	-	-	150-155	175	175

\*Figures for July 1981

#### 11. Suggested Research Program

In this section, we outline a research program which, we believe, will

- a) lead to substantial improvements in the current reduction methods; and
- b) lead to the development of a commercially viable alternate method for production of titanium.

In support of the program, we suggest that work be performed along the following lines:

- comprehensive literature survey to make a preliminary assessment of current and potential reduction methods
- preliminary laboratory experiments to determine the feasibility of the different reduction methods. These should include
  - molten salt electrolysis of chlorides and fluorides
  - electrolysis of molten oxide baths with  $TiO_2$
  - use of liquid metal electrodes (Na, Mg, and possibly, Zn or Cd) in the electrowinning of Ti
  - use of liquid metals (Na, Mg, Zn, Cd) as additives to develop the basic Kroll and Hunter processes, possibly as continuous operations
  - direct reduction of  $TiO_2$  by metals (Ca) and/or non-metals (C)
- estimation and comparison of costs involved in each of the methods listed above.

Based on this information, the most promising method will be selected for detailed investigation. This should consist of the following:

- design and construct laboratory scale equipment and carry out extensive tests on the selected reduction method
- make a detailed assessment of the factors involved in the construction of a commercial plant

- design and construct the principal components of a pilot plant on a semi-production scale
- operate the pilot plant to obtain information on the process operating parameters and to optimize the reduction method
- produce and characterize samples of titanium metal

#### Acknowledgments

The author is grateful to Professor Gerhard Jangg for very useful discussions. He would also like to thank Ms. Sue Thur and Ms. Alicia Elwin for assistance with manuscript preparation.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract #W-7405-ENG-48.

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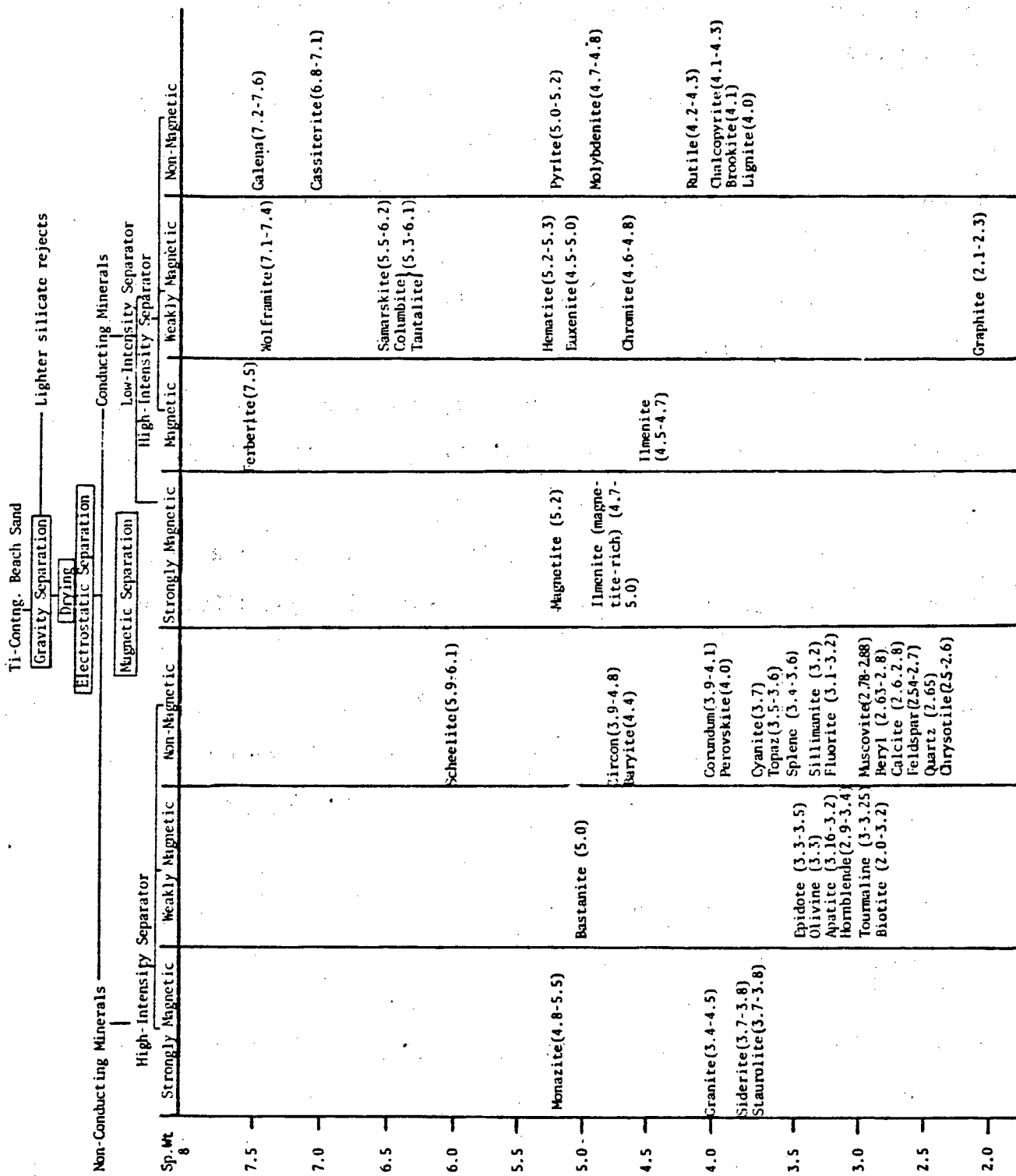


Fig. 1 Separation Response of Various Minerals in Titanium-Containing Beach Sands

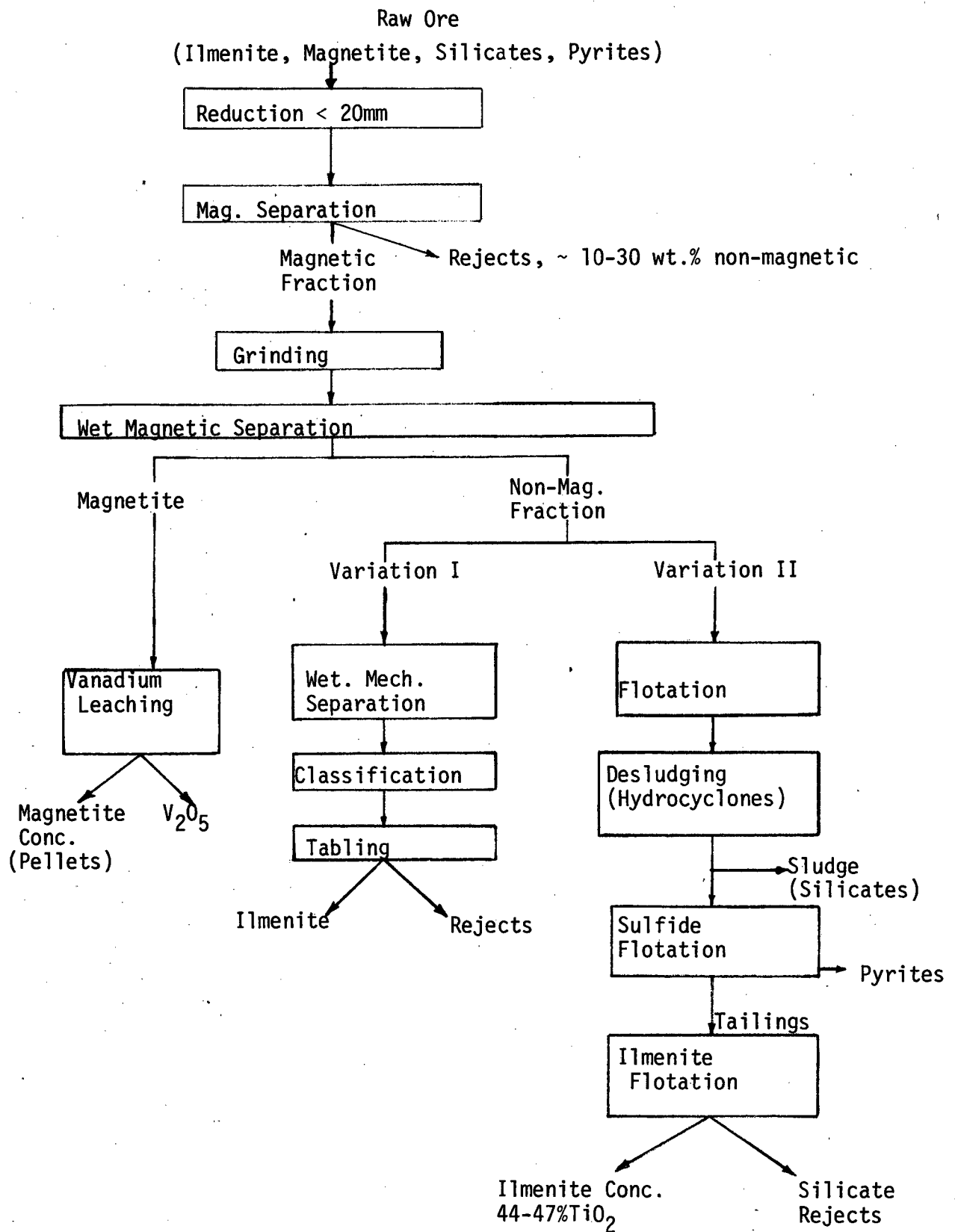


Fig. 2 General Flowsheet for the Benefication of Primary Ilmenite-Magnetite Ores

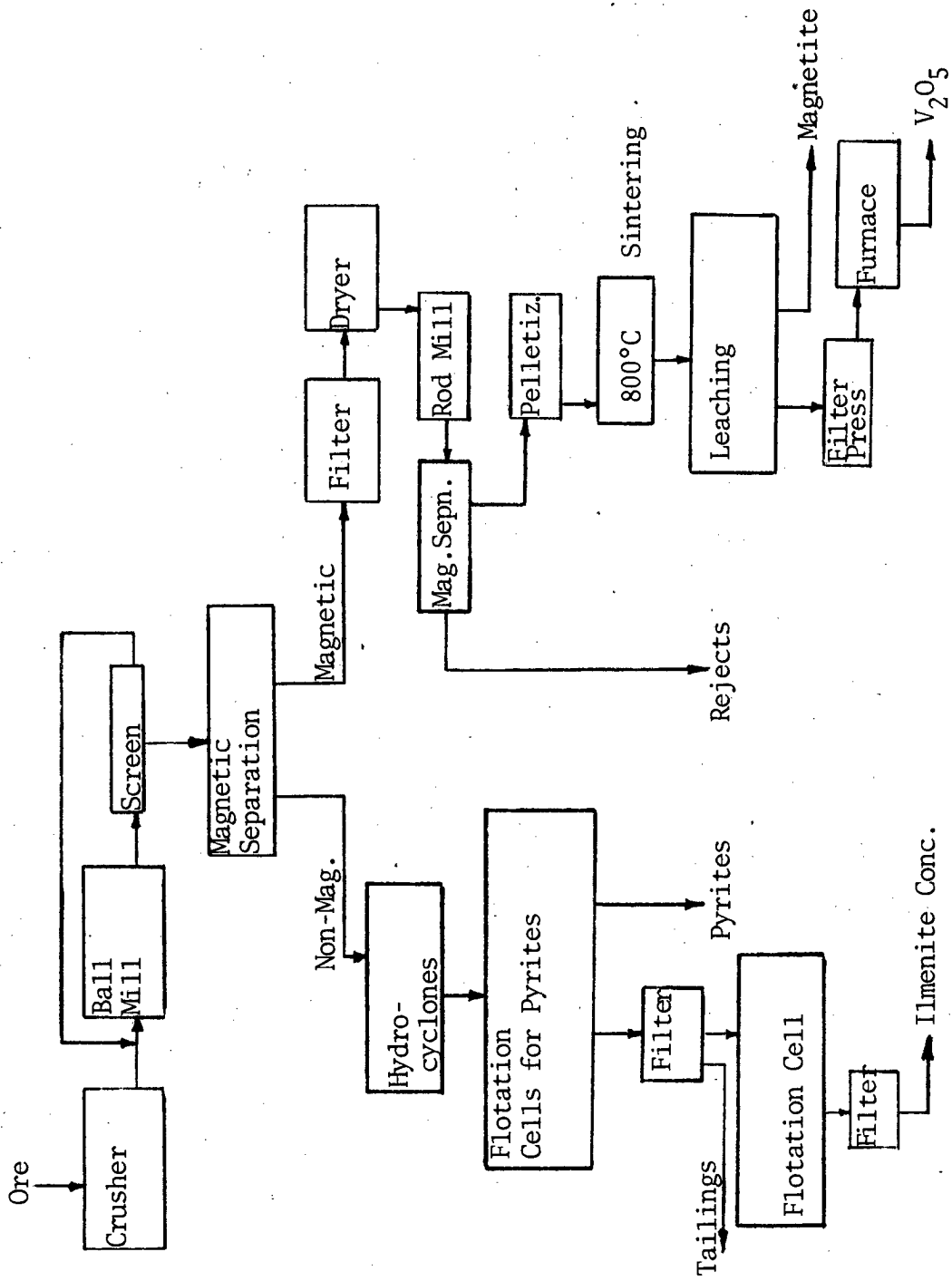


Fig. 3 Flowsheet of the Ore Benefication Process in Otanmäki, Finland

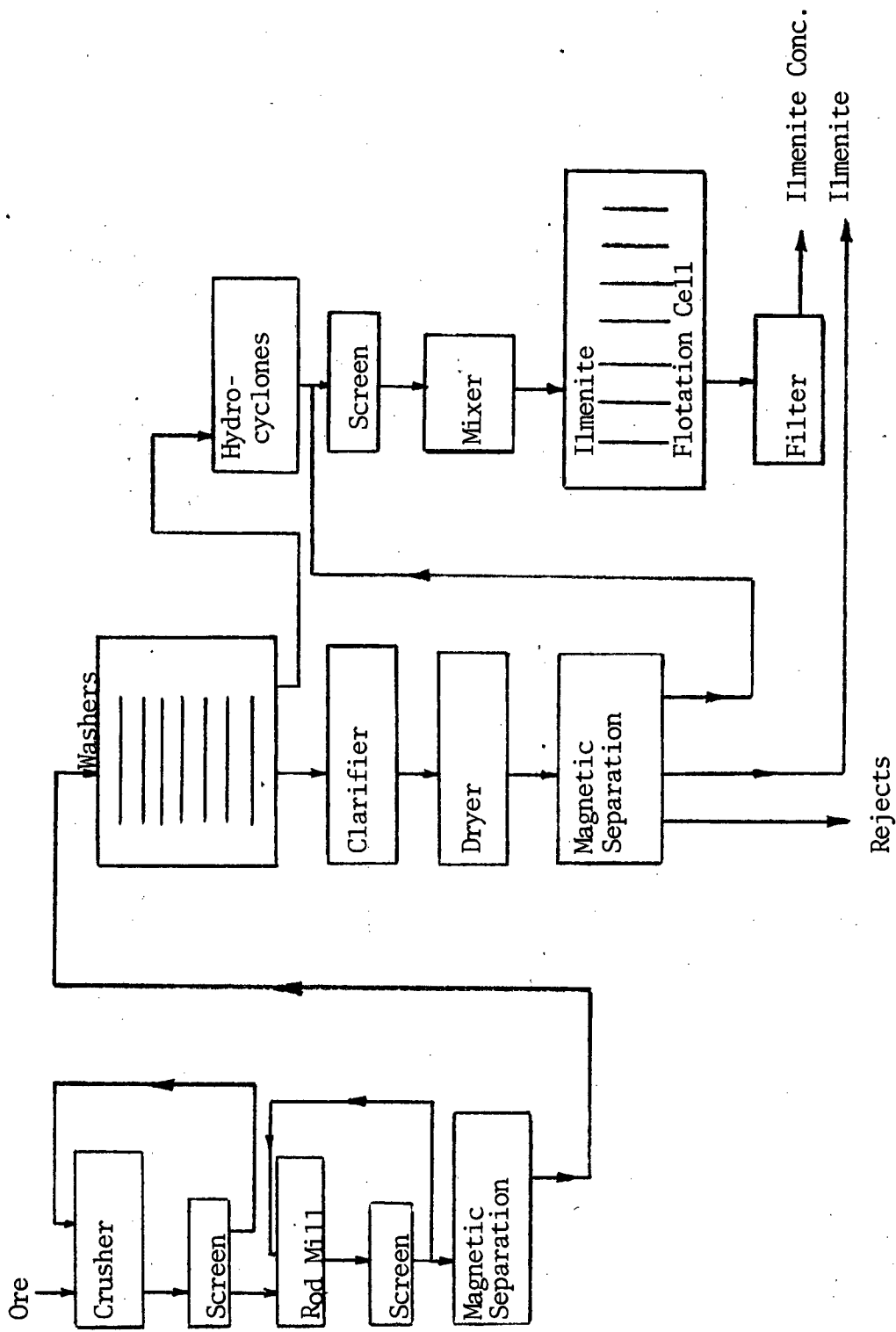


Fig. 4 Schematic Flowsheet of the Tahawus Beneficiation Plant.



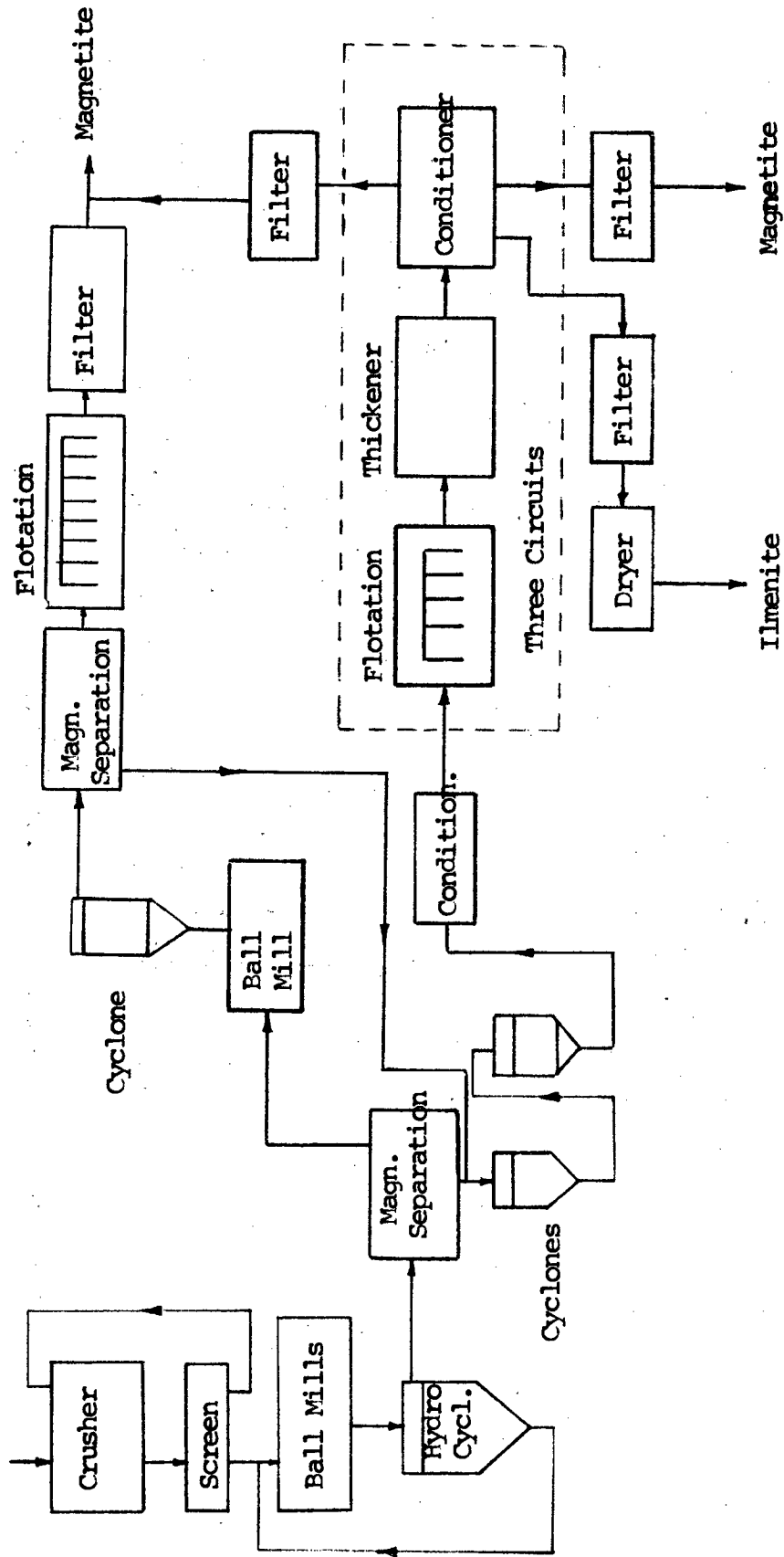


Fig. 5 Schematic Flowsheet of the Ilmenite Concentration Plant in Tellnes, Norway

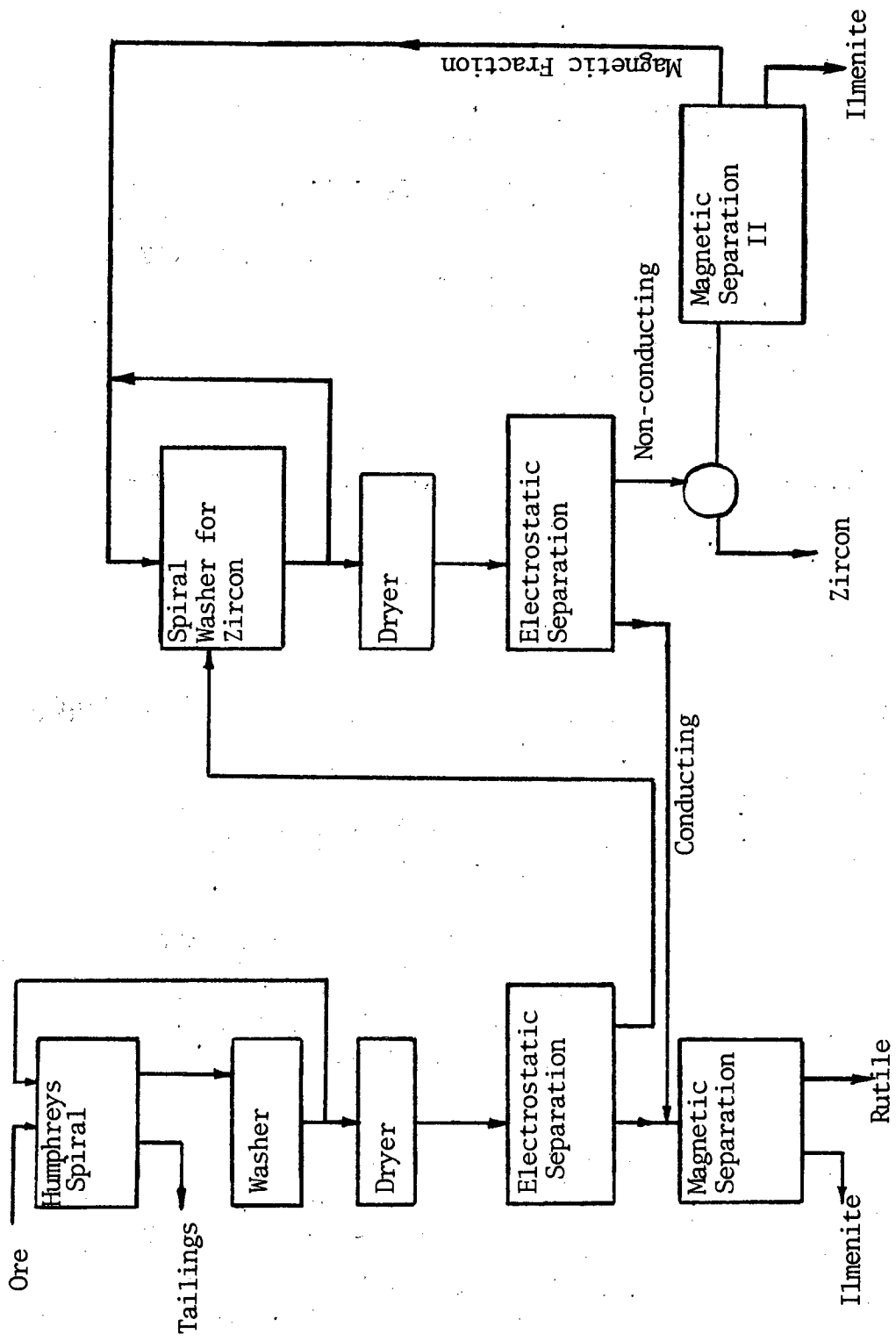


Fig. 6 Ilmenite Ore Beneficiation in Jacksonville, Florida.

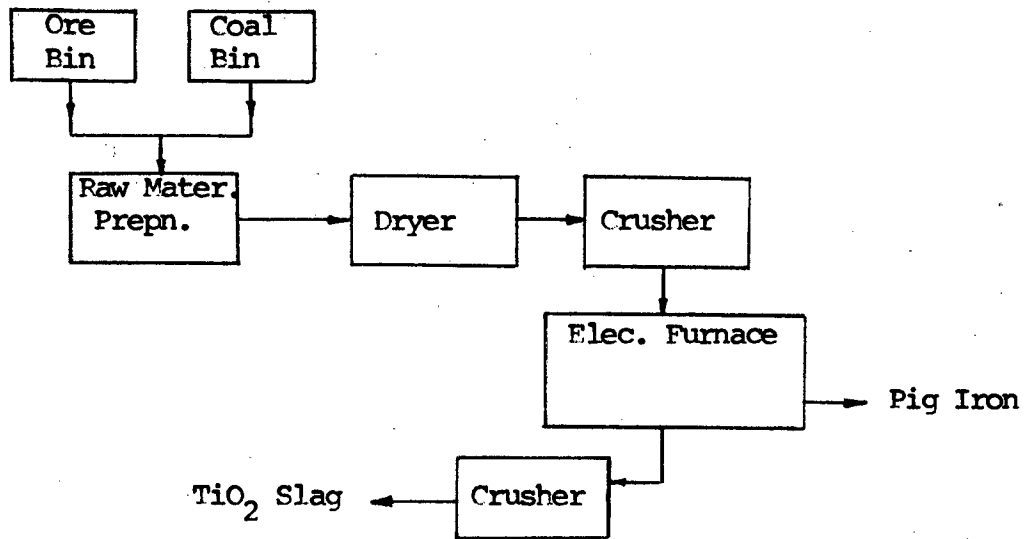


Fig. 7 Process Flowsheet for the Manufacture of  $\text{TiO}_2$  - Slag in Sorel, Canada

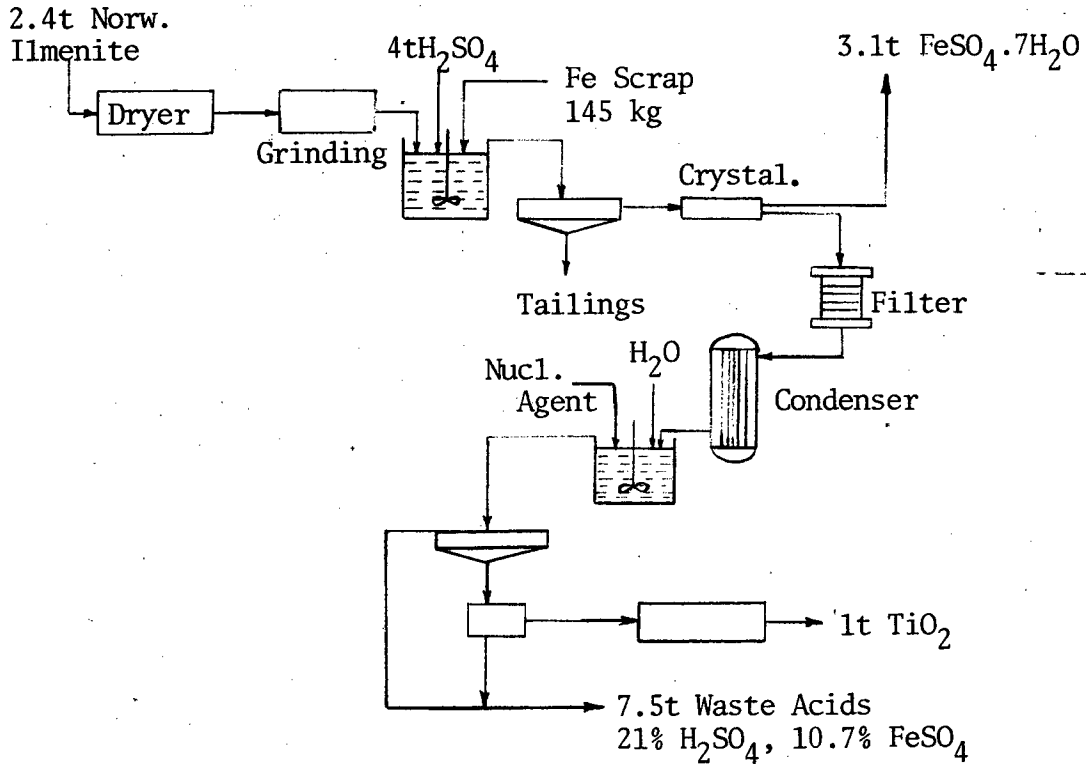


Fig. 8 Sulfuric Acid Process for the Production of  $\text{TiO}_2$ .

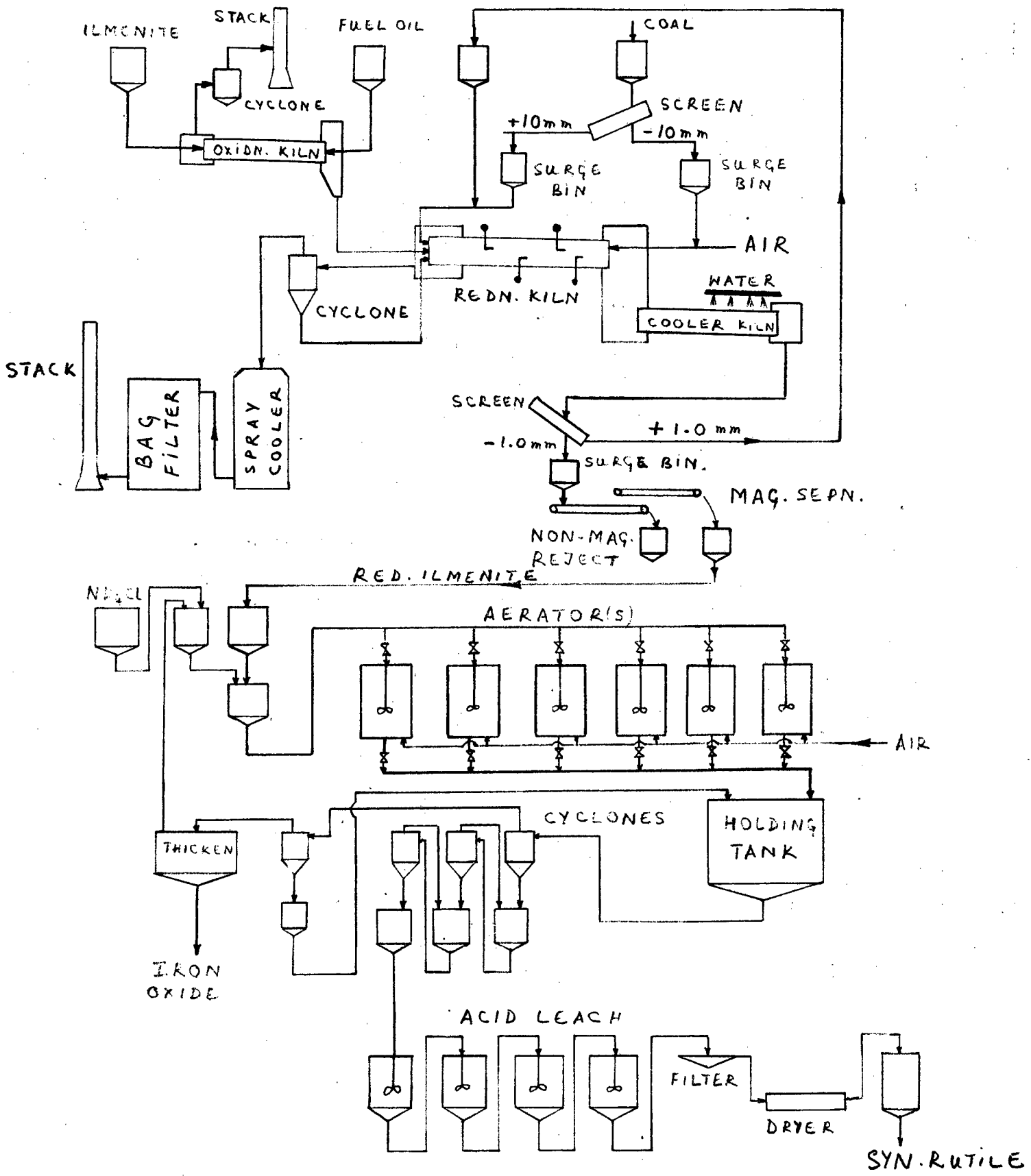


Fig. 9 Western Titanium Direct Reduction Process for Production of Synthetic Rutile.



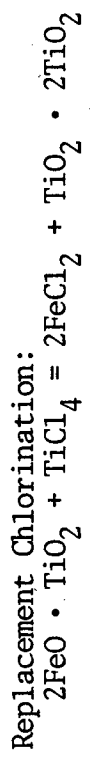
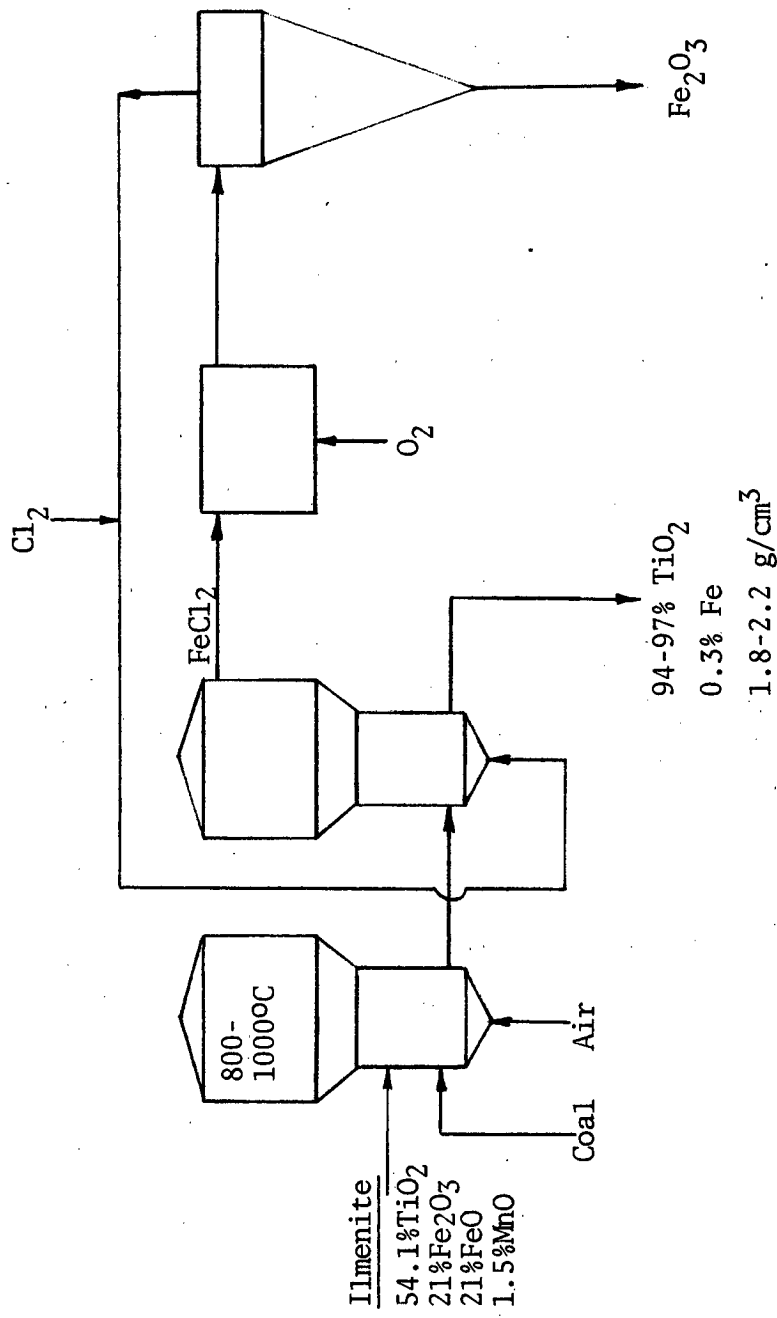


Fig. 12 Flowsheet for Preparation of Synthetic Rutile According to the Chlorine Technology Process

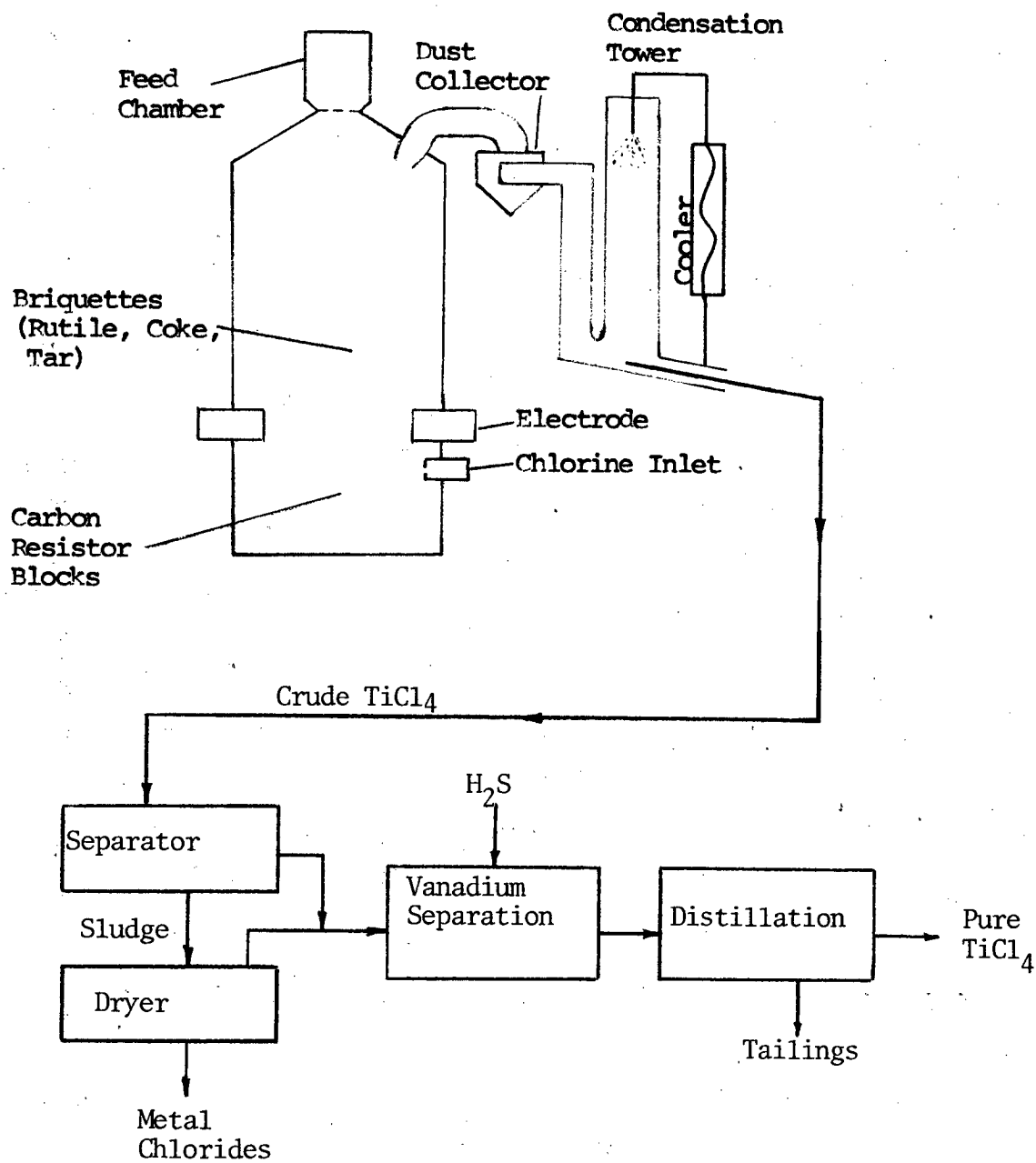


Fig. 13 Preparation and Purification of Titanium Tetrachloride

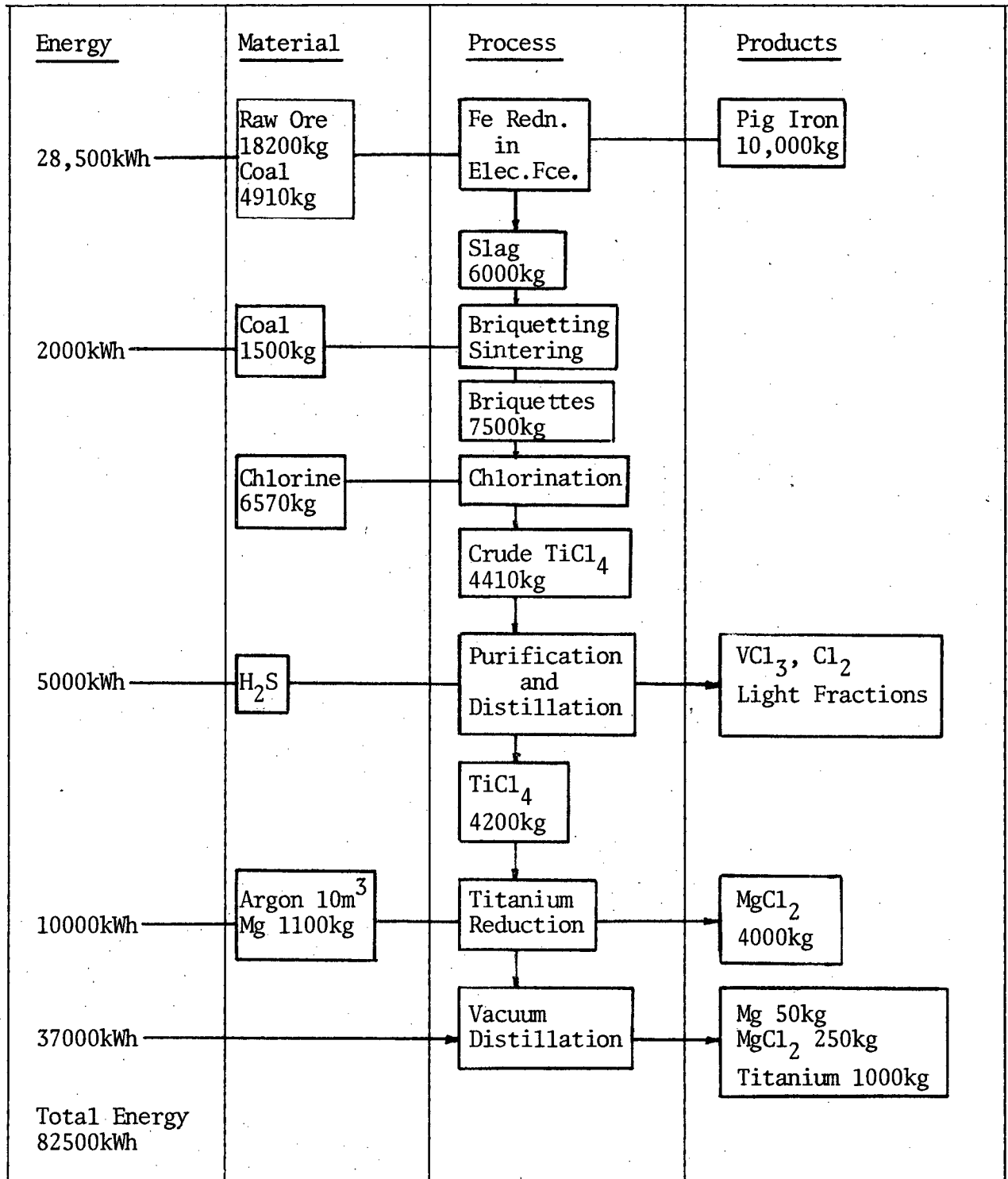


Fig. 14 Average Energy and Material Balance in the Production of 1 tonne Titanium Sponge from Ilmenite



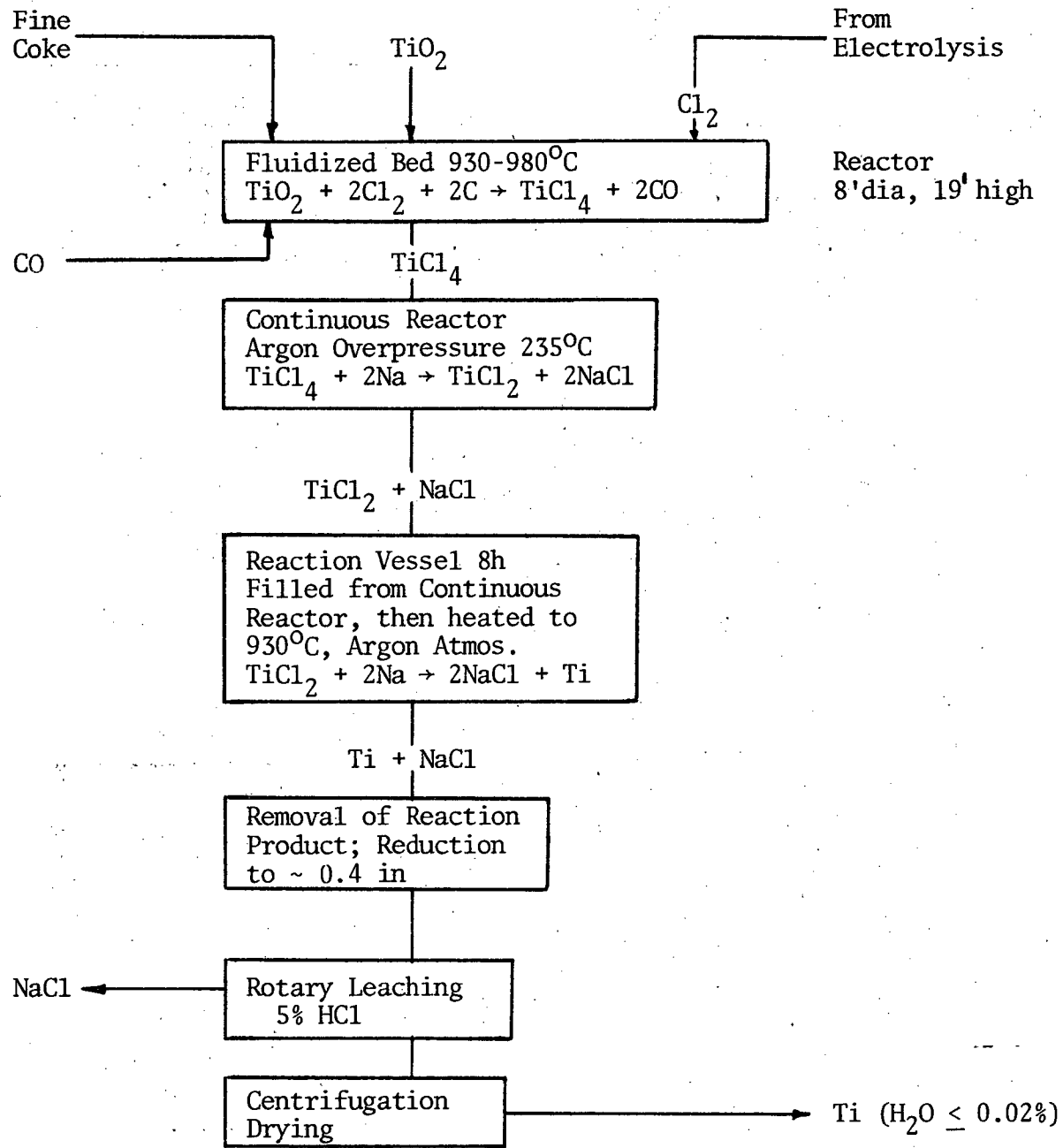


Fig. 15 Titanium Sponge Production by a Two-Stage Sodium Reduction Process

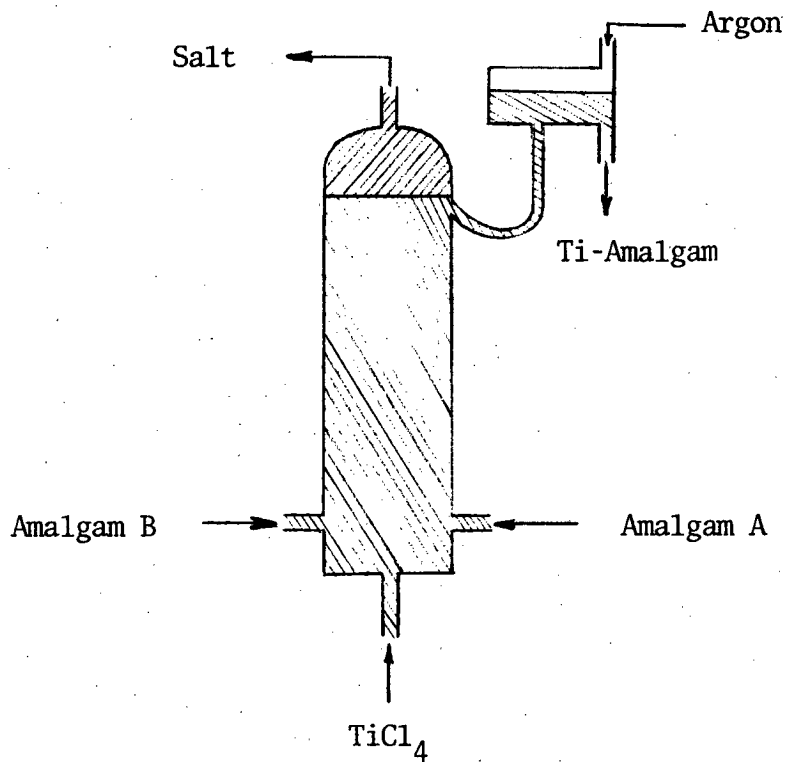


Fig. 16 Apparatus for the Separation of Reaction Products by Na-Ca Amalgam Reduction of  $TiCl_4$

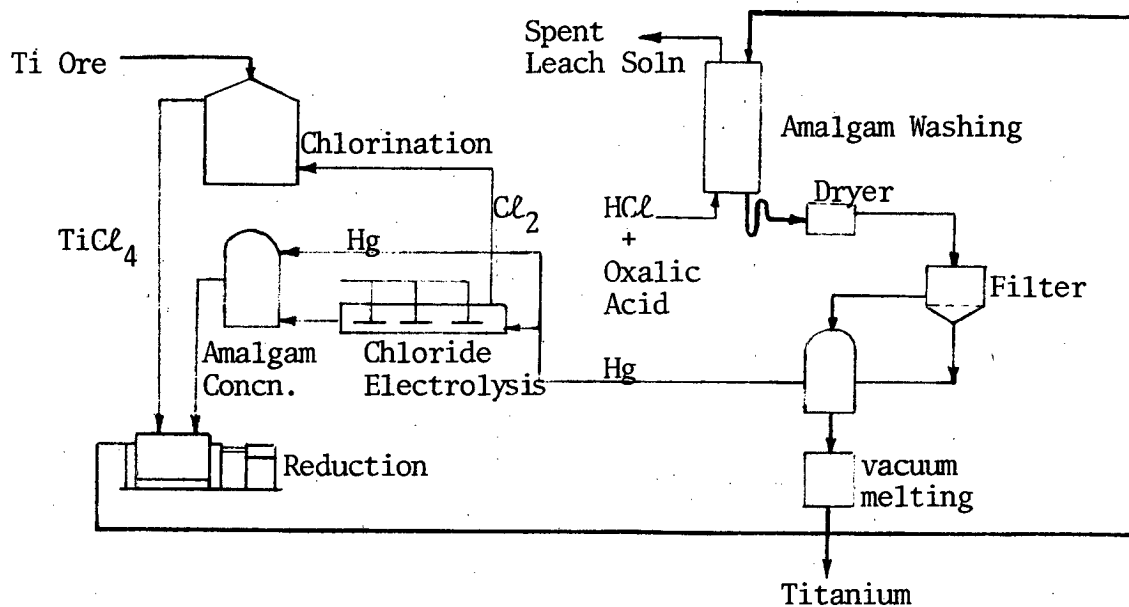


Fig. 17 Schematic Flowsheet of a Laboratory Scale Pilot Plant for Continuous Production of Titanium Sponge by Amalgam Reduction

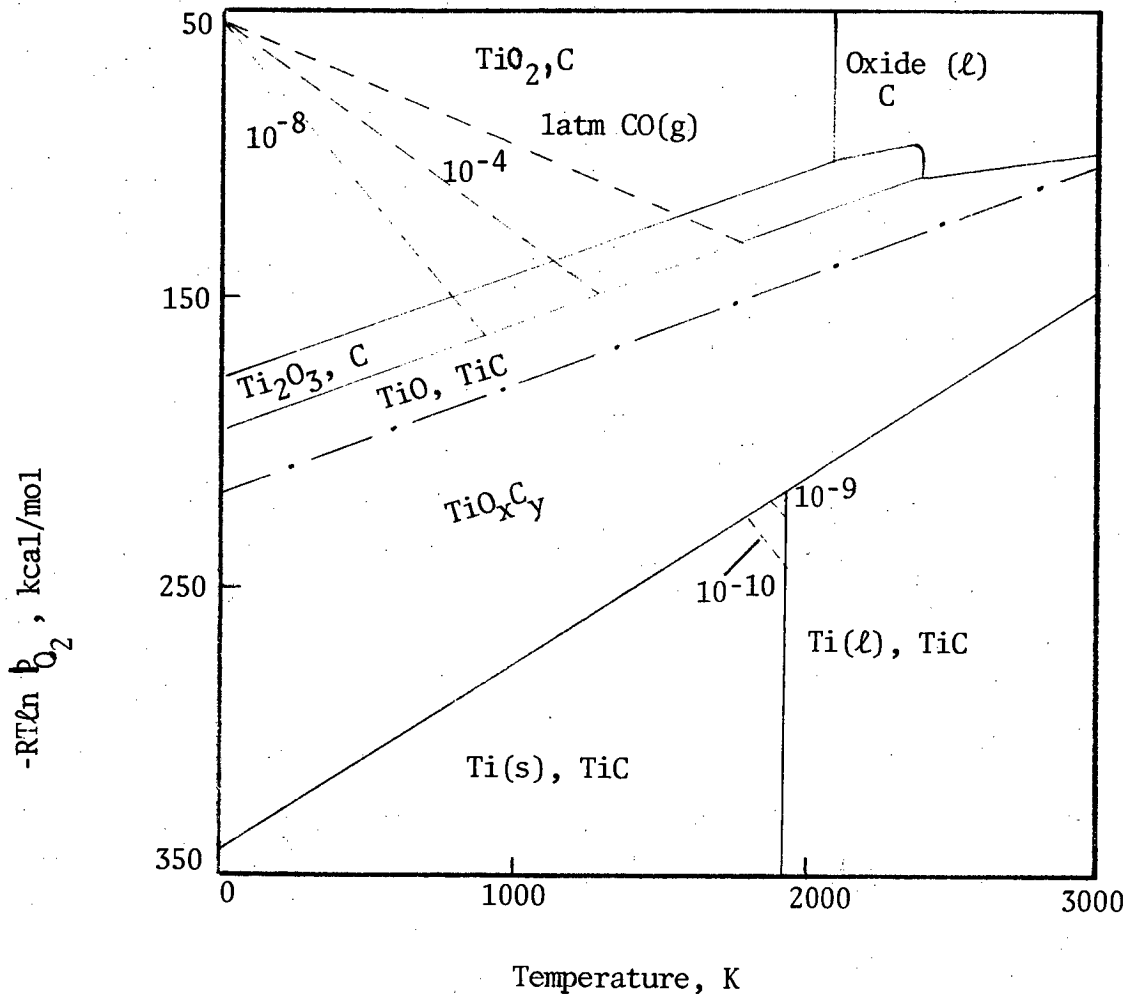


Fig. 18 Oxygen Potentials in the Ti - C - O System for Carbothermic Reduction of Titanium Dioxide

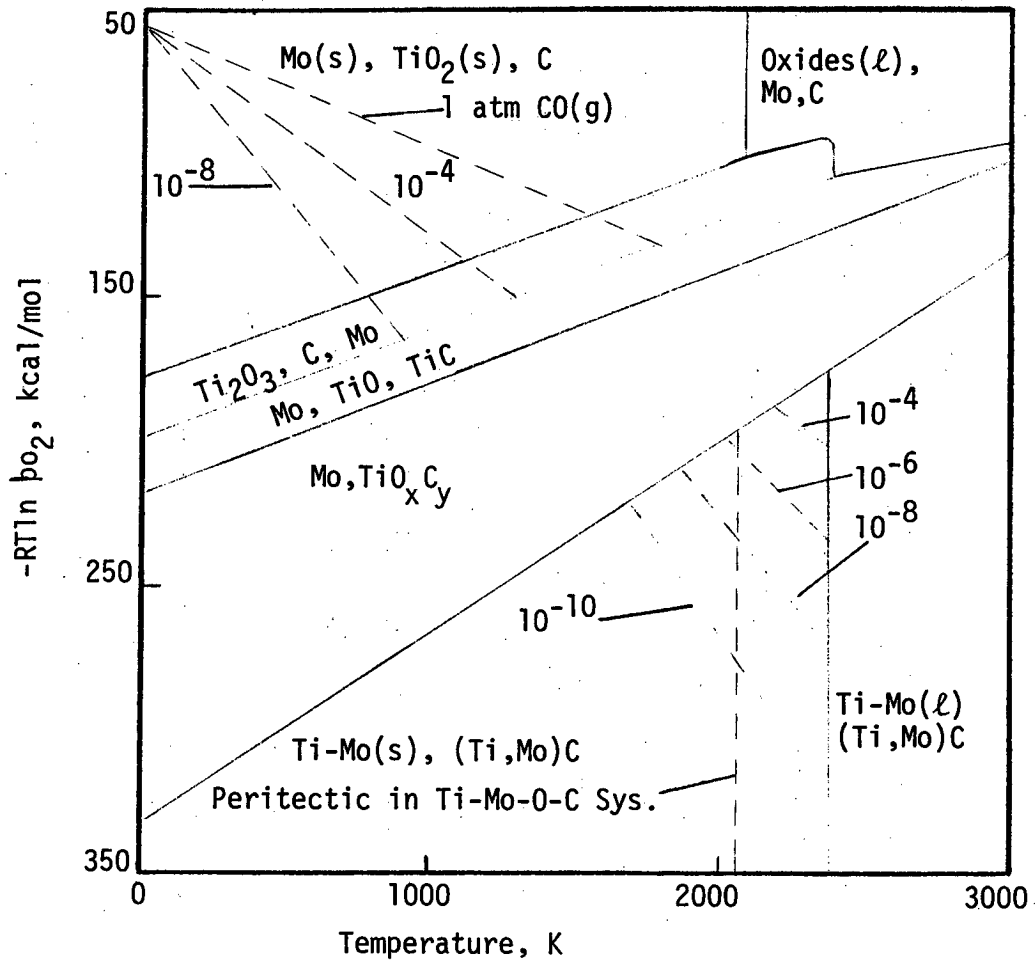
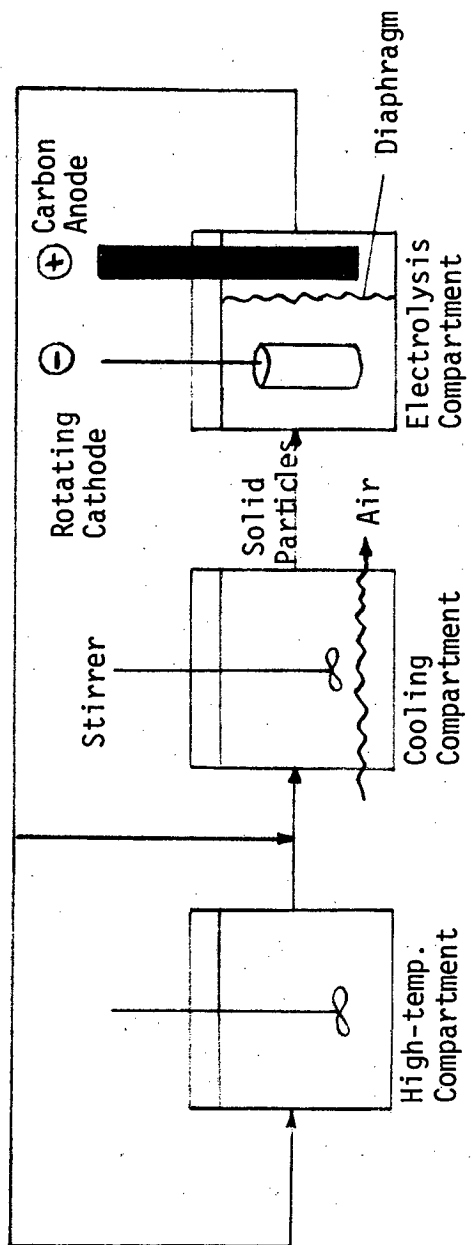


Fig. 19 Oxygen Potentials in the Ti-Mo-C-O System for Carbothermic Preparation of a 50% Ti - 50% Mo Alloy



Flow of Fused Salts

Fig. 20 Schematic Model of the Flow of the Fused Salt Electrolyte

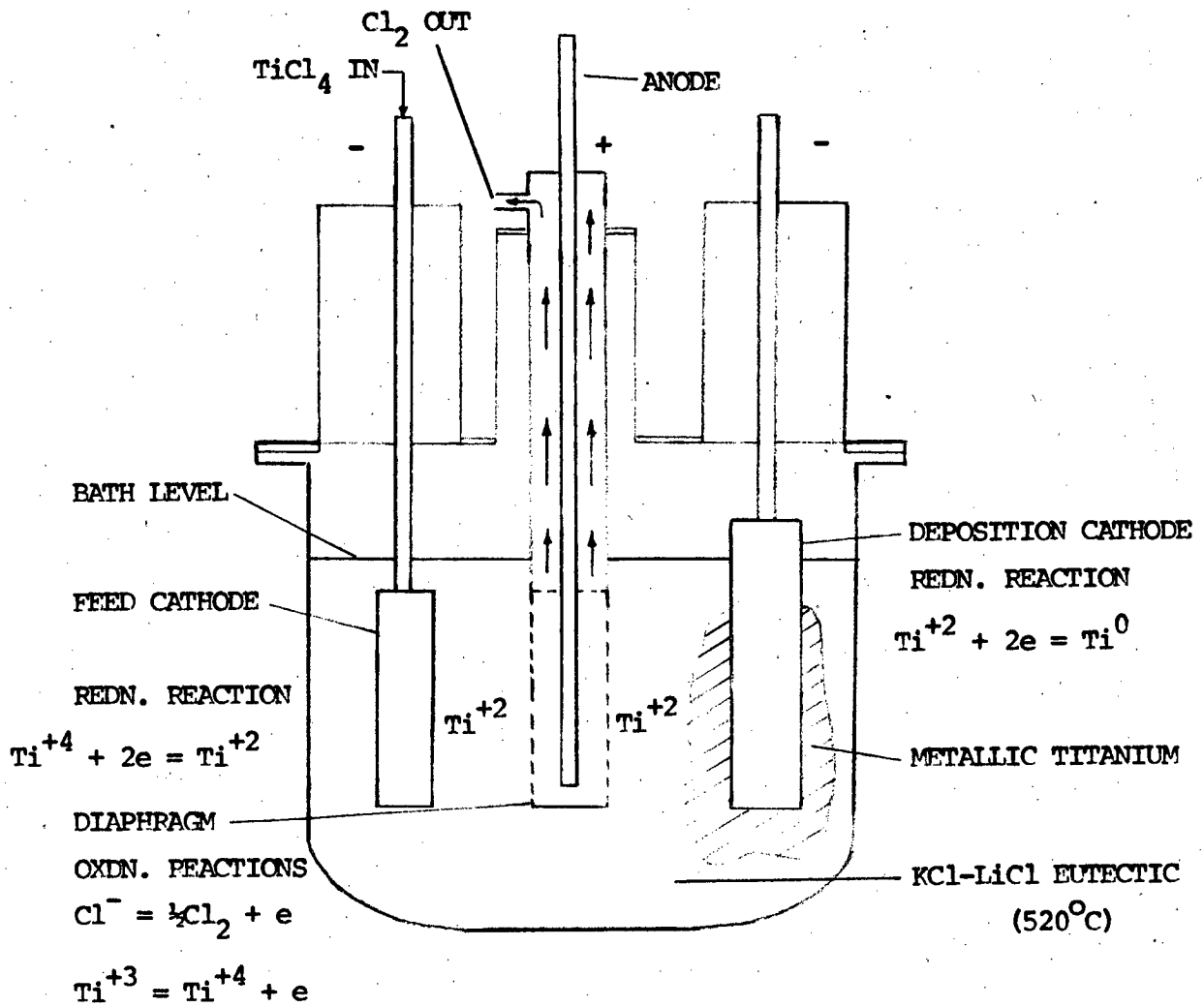


Fig. 21 Schematic Representation of the Electrochemical Cell Reactions in the D-H Company Electrolytic Process

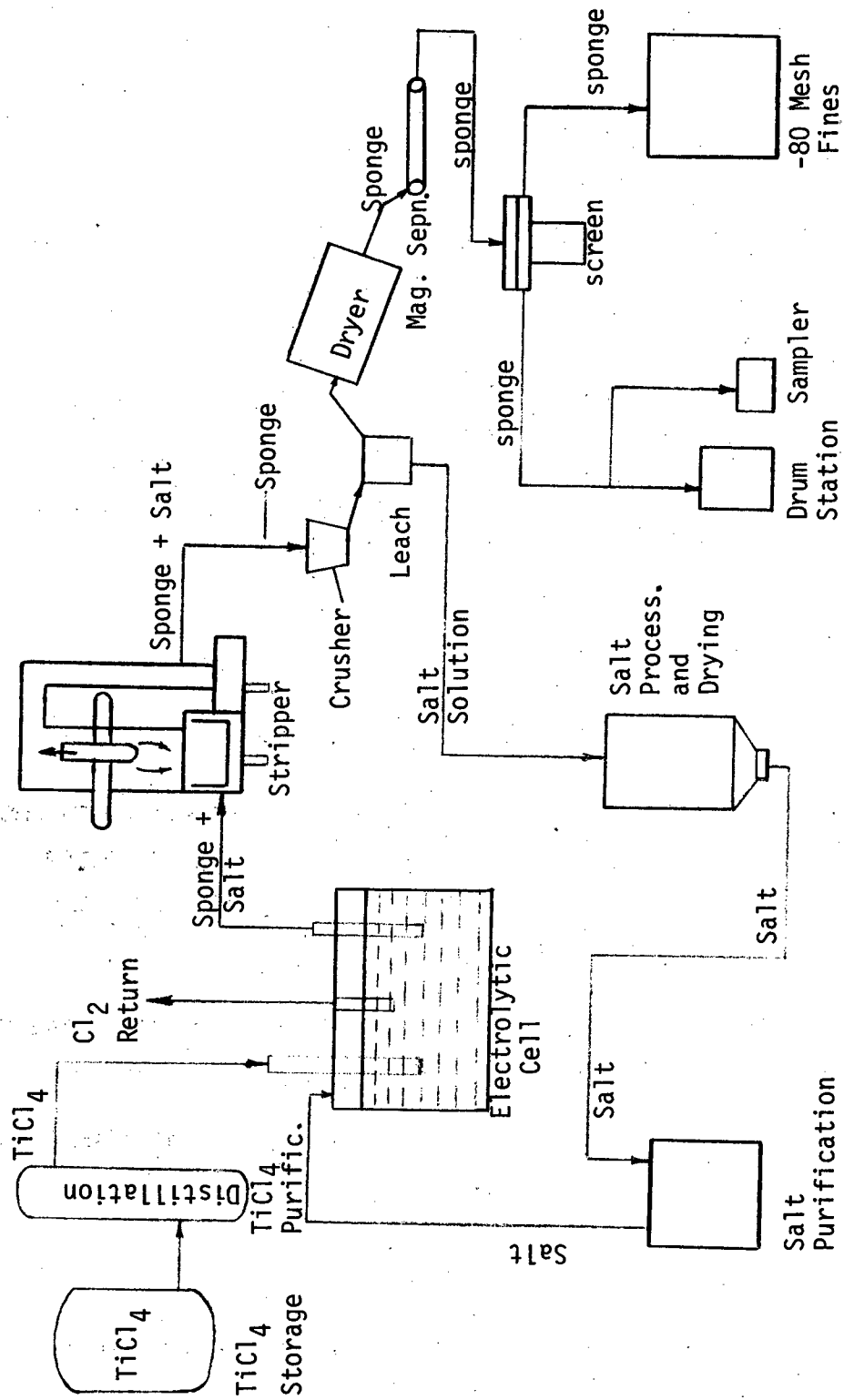


Fig. 22 D-H Company Process Flowsheet for Electrolytic Production of Titanium Sponge

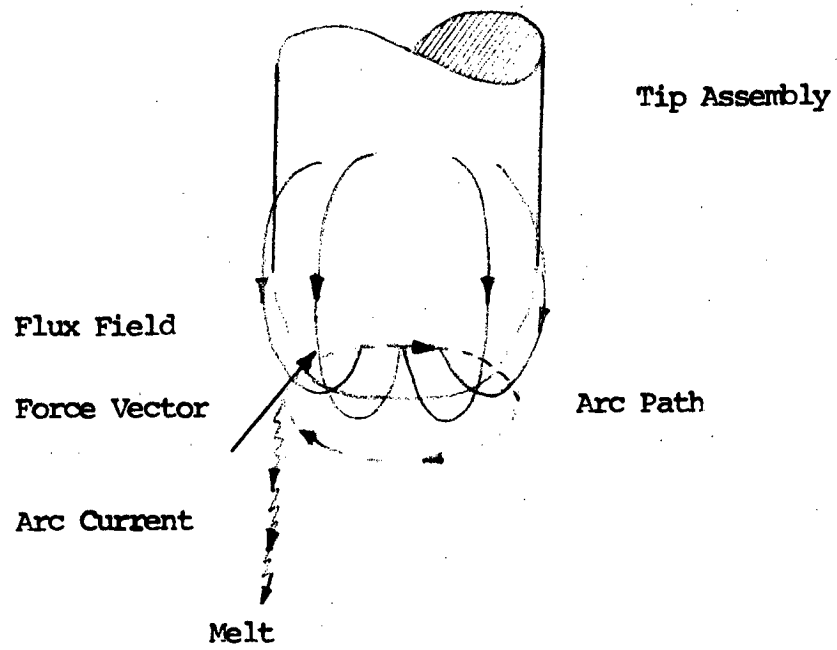


Fig. 23 Arc Rotation on a Durarc Electrode



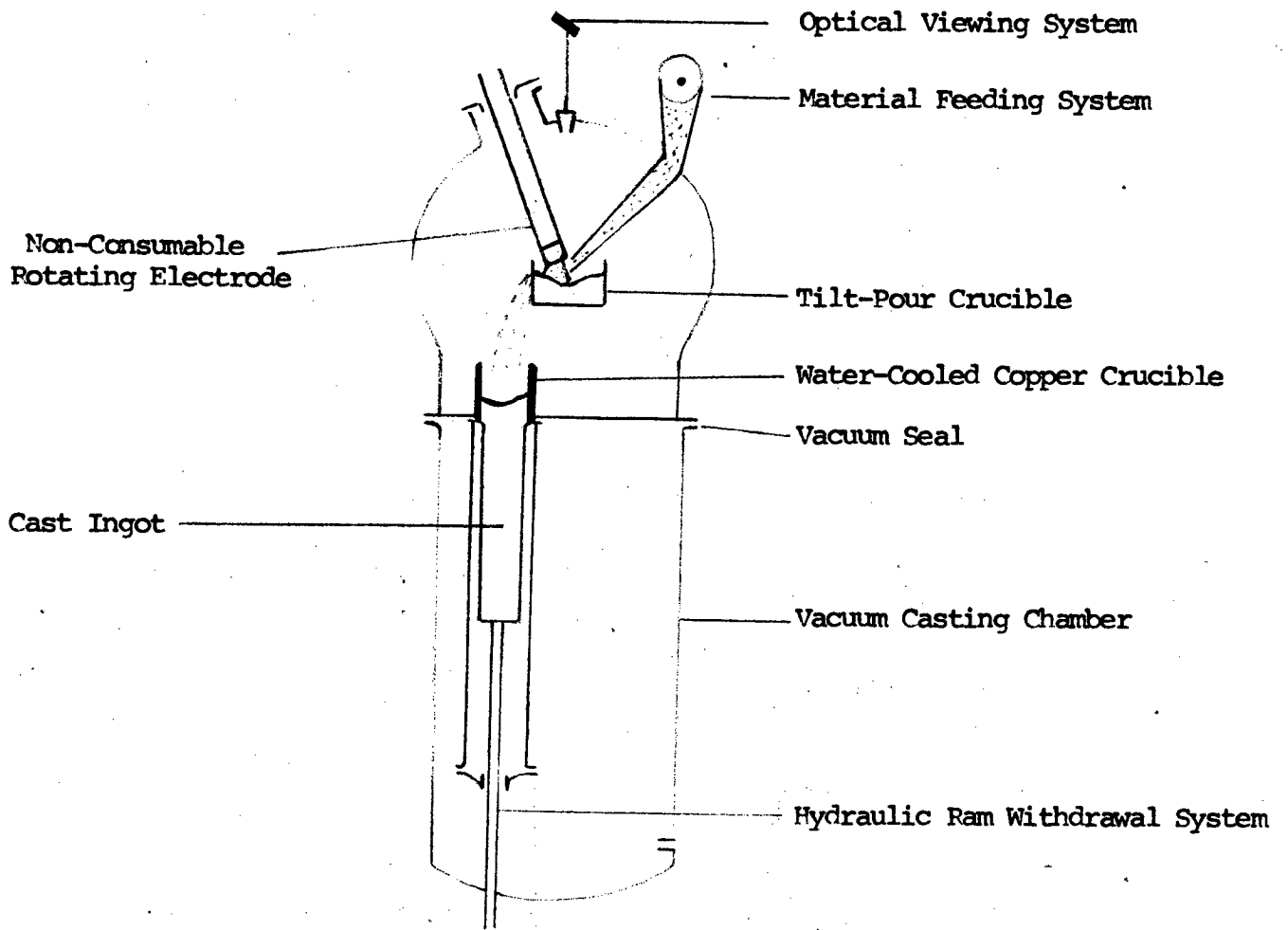


Fig. 24 Rotorode Nonconsumable Arc Melting Process

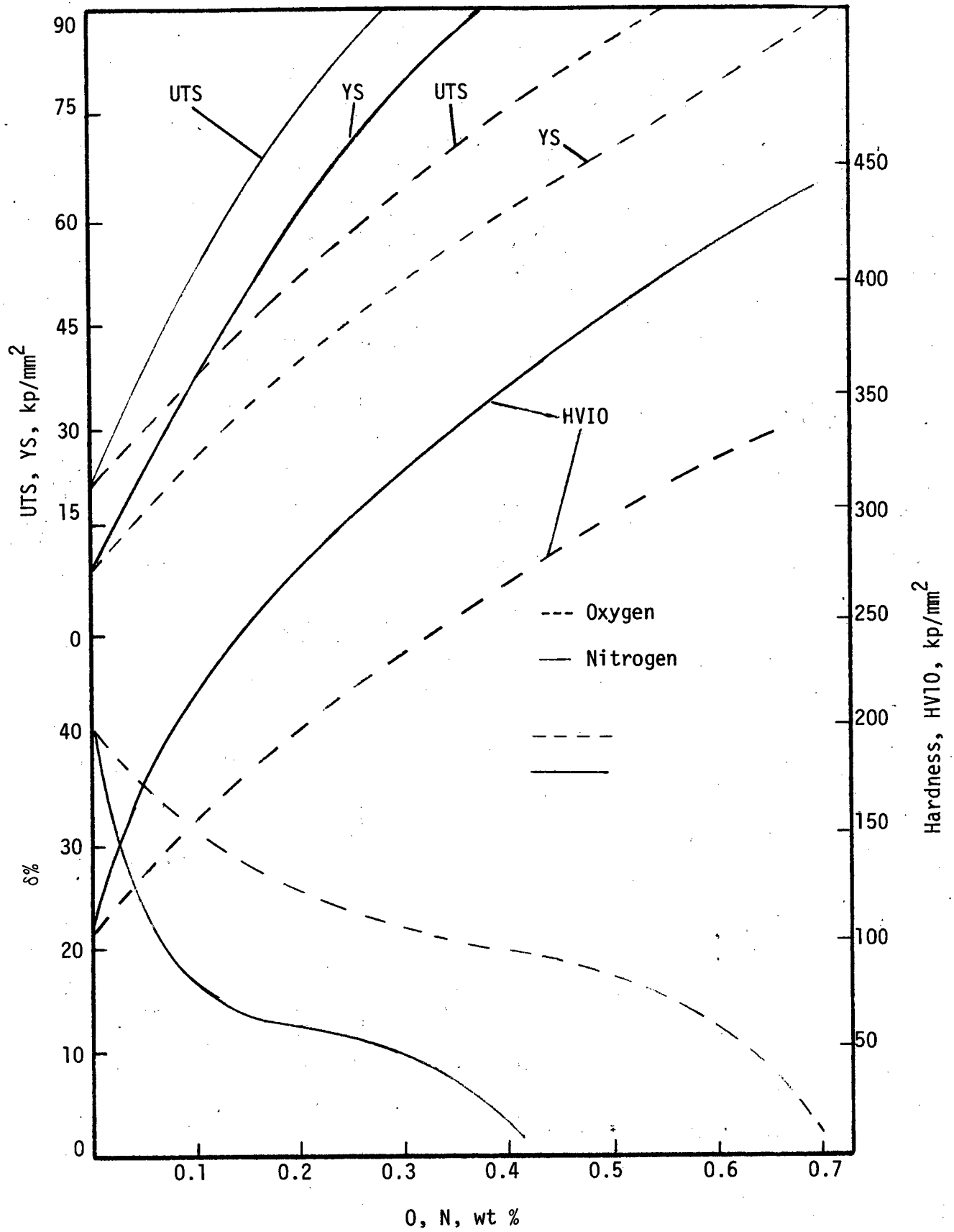


Fig. 25 b Effect of Oxygen and Nitrogen on the Room Temperature Mechanical Properties and Hardness of Titanium

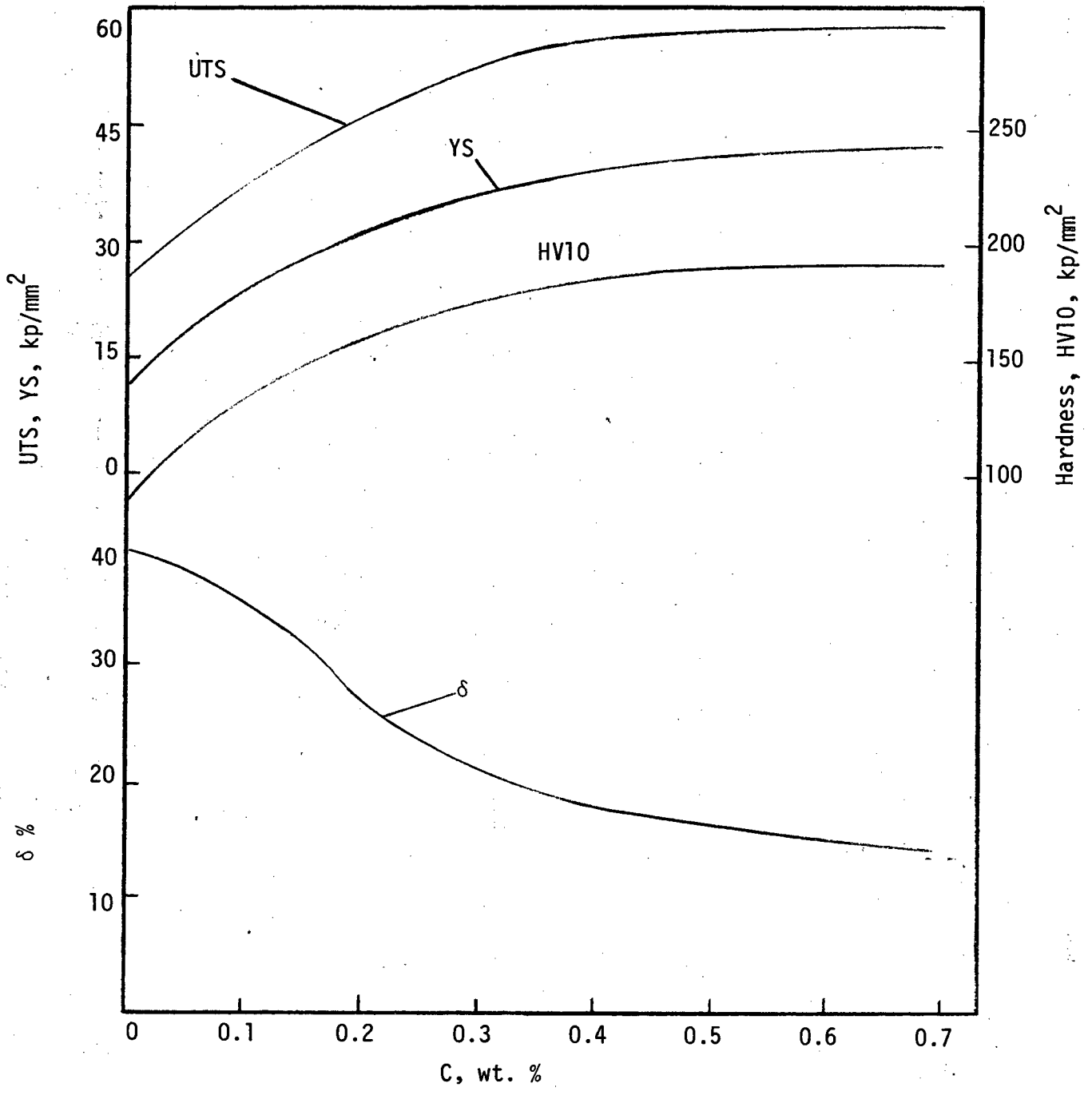


Fig. 25a. Effect of Carbon on the Room Temperature Mechanical Properties and Hardness of Titanium

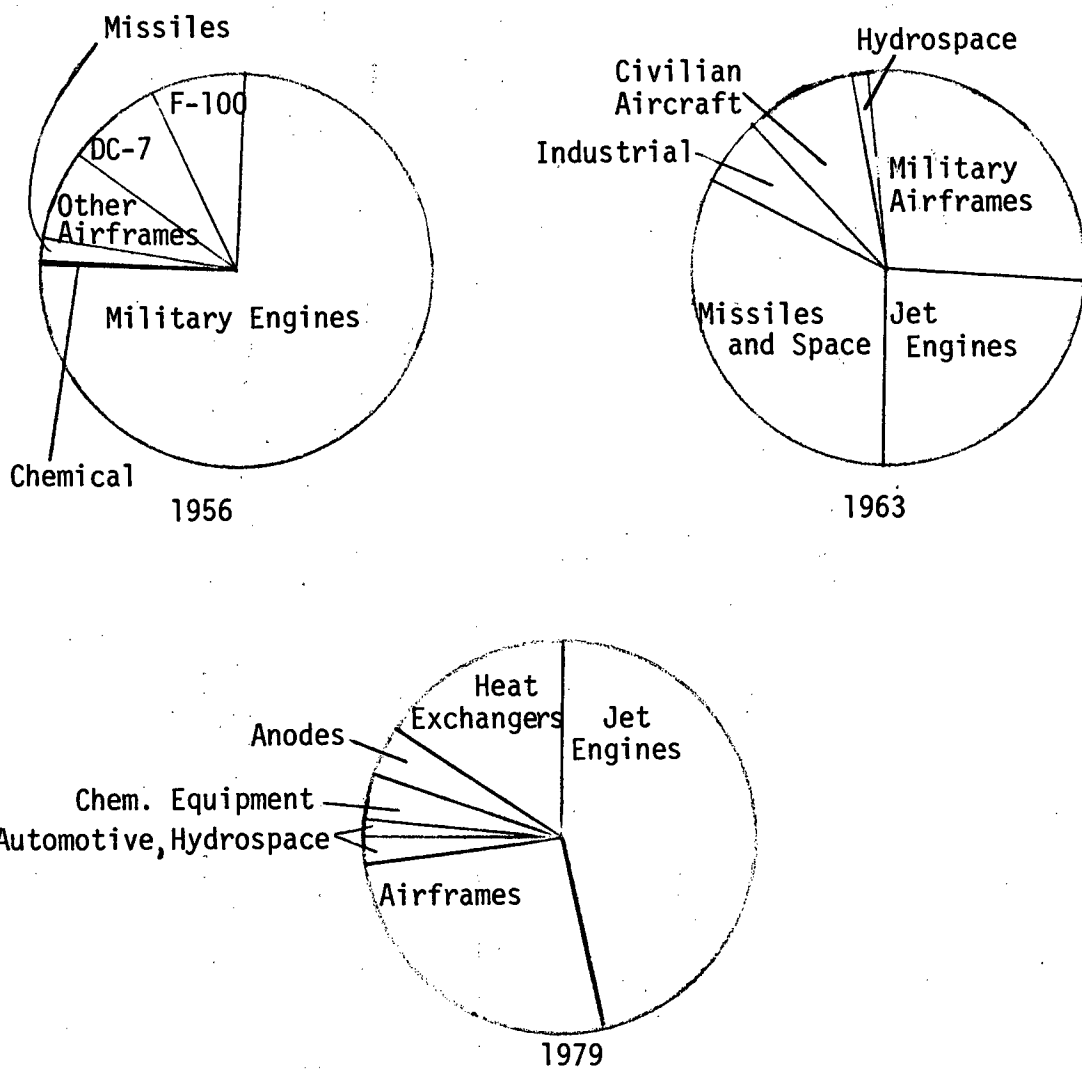


Fig. 26 Market Distribution of Titanium

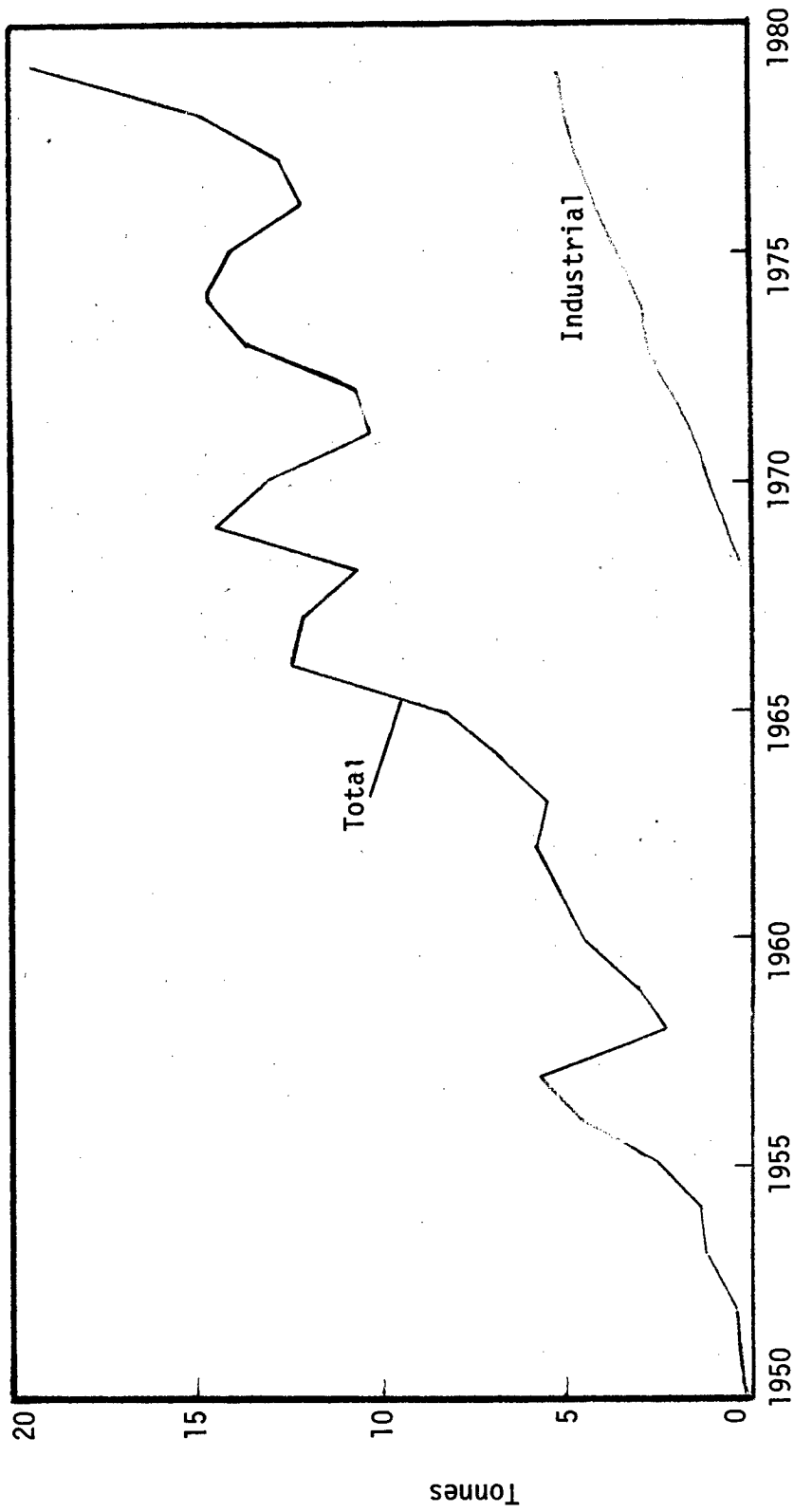


Fig. 27 U.S. Titanium Mill Products Total and Industrial Shipped Annually

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