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Development of Technology for Large Scale Production of Titanium Sponge

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Abstract. Intensive investigations on the development of titanium metal production technology had been carried out during 1965-1975 at the Bhabha Atomic Research Centre, Bombay and at the Nuclear Fuel Complex, Hyderabad. The Defence Metallurgical Research Laboratory, Hyderabad has set up a 'Titanium Sponge Experimental Facility' with a capacity to produce 100 tonnes of sponge per annum in 2000 kg batches by the Kroll's process with a view to optimising technology for large scale production.

The paper presents an outline of the experimental facility and discusses the various considerations that have gone into the design of equipment, materials of construction, process selection, etc. The facility has gone into operation in March, 1985. The results obtained so far are encouraging.

1. Introduction

Production of titanium sponge in 15 lb batches commenced in 1946 at the Bureau of Mines Albany Plant in the USA. This was followed by 100 lb batch size operations in 1949 at the National Lead Works, USA. The metal was produced by the magnesium reduction/vacuum distillation route pioneered and perfected by Dr. W.J. Kroll at Albany. Since then, extensive investigations have been carried out all over the world to improve upon this original process and to innovate new techniques of manufacture. A number of patents' have been taken and massive literature[2,3] has been generated.

The current world production capacity for titanium sponge is estimated at 1,20,000 tonnes per annum, the bulk of it being produced in the USA, USSR and Japan*. Because of a quantum jump in the installed capacities during 1979-8 1 period coupled with the general world-wide recession, particularly in the aerospace and power generation industries in subsequent years, the capacity utilisation is presently not at an optimum level. However, the trend of overall growth is estimated to continue at a 5-7 per cent growth rate in the coming years.

India is endowed with large resources of titanium and yet the metal is not produced in the country although commercial facilities for mineral beneficiation, pigment production, production of titanium and titanium alloy mill products and fabricated engineering equipment are in regular operation. Large scale production of titanium metal is at present limited to only a few advanced countries mainly on account of the highly sophistciated technology required for its extraction from the minerals. However, to meet the growing demand[5] for the metal in India (Fig. 1) there is an urgent need to set up a commercial plant.

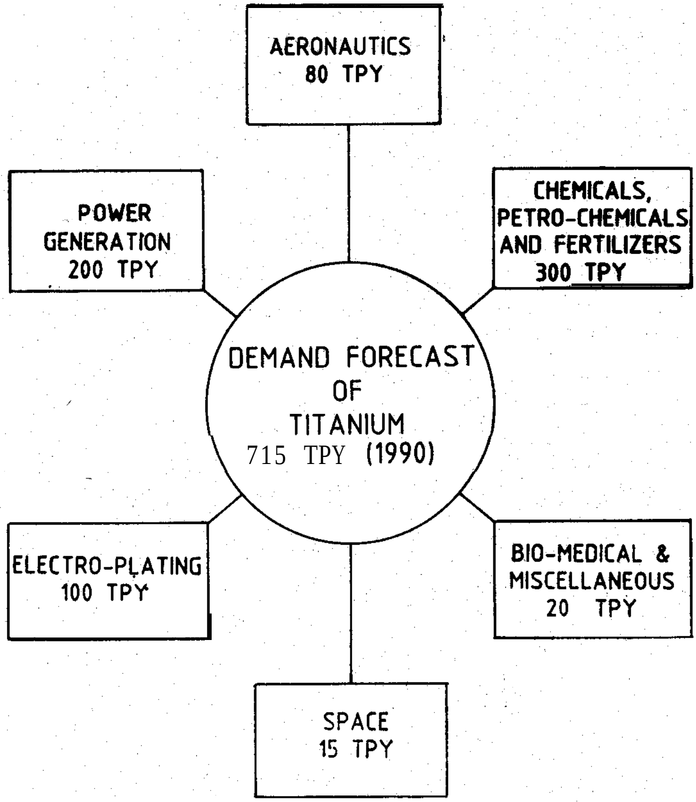

Figure 1. Demand forecast of titanium in India (1990).

2. Current Status on Production Technology

Currently, large scale production of the metal is carried out in batches either by the Kroll's or by the Hunter's process. The Kroll's process in its improved and refined form is the favoured method (Table 1) for commercial production of sponge, while the

Table 1. Processes for the production of titanium sponge and annual world production capacity.

Process	Capacity (Xl000 tonnes)
Mg Reduction-Vacuum Distillation	84.6
Mg Reduction-Aqueous Leaching	14.5
Mg Reduction-Argon Gas Sweeping	4.1
Na Reduction-Aqueous Leaching (Single Stage)	5.0
Na Reduction- Aqueous Leaching (Two Stage)	10.0
Fused Salt Electrolysis of $TiCl_4$	Nil
Total	118.2

Hunter's process of sodium reduction of titanium tetrachloride is practised only in a limited way. The third process, viz., the fused salt electrolysis of titanium tetrachlbride, has not yet emerged as a commercial alternative. The only commercial venture proposed by this route by D.H. Titanium, USA is reported to have been shelved for the present mainly due to a steep decline in the demand for the metal.^{6}

The basic reaction involved in the magnesiothermic reduction process is

$$TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$$

The reaction, however, may occur in stages, i.e.

$$TiCl_4 + Mg \rightarrow TiCl_2 + MgCl_2$$

$$TiCl_2 + Mg \rightarrow Ti + MgCl_2$$

Formstion of $TiCl_3$ may also take place. $TiCl_2$ has higher solubility in $MgCl_2$ and hence enters the melt and gets reduced to metal, while $TiCl_3$ escapes and settles in the cooler zones of the reaction vessel. In the absence of sufficient *Mg*, $TiCl_4$ also reacts with *Ti* to from lower chlorides. Hence, in the process always excess *Mg* is used which is separated by vacuum distillation. The process is exothermic and hence at higher feed rates of $TiCl_4$ the reaction temperature is required to be controlled by removal of excess heat. The mechanism of the process is not well understood though it is generally known that heat transfer rate and sponge growth phenomena affect the rate of the reaction, metal yield and its quality.

Major steps in the production of titanium sponge from rutile are depicted in (Fig. 2). Till date large scale production of titanium sponge has essentially remained a batch process for several reasons, such as stringent operating conditions of temperature and process environment, high melting point of titanium and its high reactivity, strongly

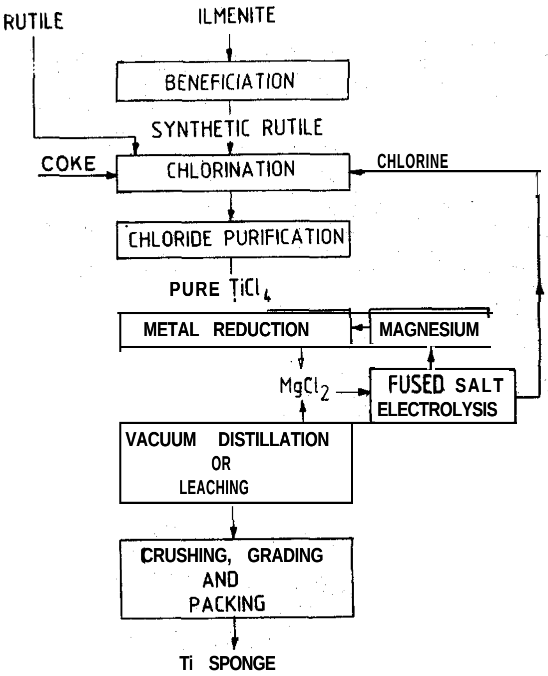

Figure 2. Major steps in the production of titanium sponge.

adhering nature of titanium sponge to the reduction pot etc. Commercially the metal is produced in batches of 1-5 tonnes capacity. Though batch sizes of 7-8 tonnes have recently been mentioned in the literature, from the quality point of view, it is reported that the metal made in 2-5 tonne batches is preferred presumably due to problems in separating the by-products from sponge in larger batches as well as the complex nature of equipment required for the subsequent handling of the metal. Reduction reactors of both vertical and horizontal types have been tried.' Vertical reactors are preferred for smaller batch sizes while for larger batch sizes horizontal reactors are reportedly in use.

2. 1 By-products Separation

For the separation of sponge from excess magnesium and the by-products magnesium chloride, three different processes viz,, (i) vacuum distillation, (ii) acid leaching and (iii) inert gas sweep followed by leaching are currently practised. While the American producers have opted for the latter two techniques from capital cost considerations, the Japanese producers have almost exclusively gone in for vacuum distillation since this process gives consistently good quality metal, TI MET, the largest producer of titanium sponge in the USA, has optimised a continuous acid leaching process, while OREMET, USA has adopted the argon sweep technique followed by leaching for by product separation. It is pertinent to note that separation of by-product from sponge produced by the sodium reduction and the electrolytic routes is necessarily to be carried out by the acid leaching techniques only.

2.2 Material of Construction

High temperature operation, aggressive and oxidising media, tendency for the reductant and the product metal to react with the reactor material have led to a limited choice in regard to materials of construction for the reduction retorts. Stainless steel are generally preferred although for specific and limited applications use of carbon steels have also been reported. While reduction retorts fabricated from medium carbon steels are generally compatible with the reactants and products, the exothermicity of the reduction reaction, coupled with the high temperature operation, very severely limits the operating life of such reactors. On the other hand, austenitic stainless steels pose a compatibility problem with the reductant since liquid magnesium is known to leach out nickel from such grades of steel at the high operating temperature. Such reactors therefore need to be protected with ferritic stainless steel liners.

2.3 Heating Equipment

For heating the reduction retorts, oil/gas fired furnaces as well as electric resistance heated furnaces are in use although electric resistance furnaces are prefered since temperature control is much more precise in such furnaces. However, for carrying out the vacuum distillation operation, electric resistance heated vacuum furnaces are almost exclusively used.

2.4 Energy Inputs

Production of titanium metal is energy intensive, calling for an input of about 25 KWH per kilogram of sponge[6]. Several efforts towards conservation of energy are reported in literature mostly relating to the development of combined reduction/distillation processes, but none have found widespread commercial acceptance so far due to complex technological problems associated with such designs. In integrated plants, however, the liquid magnesium chloride tapped out during reduction is fed to the electrolytic cells as such, leading to a sizeable saving in energy,

3. Technology Developments at DMRL

In the initial stages of development at Bhabha Atomic Research Centre, Bombay, (BARC) and Nuclear Fuel Complex, Hyderabad, (NFC)[8-10], all the three alternatives viz., Kroll, Hunter and the electrolytic processes were investigated (Table 2). Results of these studies have formed the basis for the selection of the Kroll process for further development on a larger scale. The pilot plant at NFC has already optimised this process on a 100/120 kg batch size of titanium.

Table 2. Titanium development in India.

Year	Institution/Laboratory	Process Used	Production Capacity per batch (kg)
1953	NML Jamshedpur	*Mg* Reduction-Leaching	0.5
1967	BARC Bombay	*Mg* Reduction-Vat. Distillation	1.0
1972	BARC Bombay	*Mg* Reduction-Vat. Distillation	15.0
1973	BARC Bombay	*Na* Reduction-Leaching	5.0
1975	NFC Hyderabad	*Mg* Reduction-Vat. Distillation	100.0
1976	NFC Hyderabad	Na Reduction-Leaching	60.0
1978	NFC Hyderabad	*Na* Reduction-Leaching	120.0
1979	BARC Bombay	Electrolytic - Leaching	5.0
1984	DMRL Hyderabad	*Mg* Reduction -Vac. Distillation	2000.0

3.1 Process Flow-Sheet

The process flow-sheet, equipment selection and the batch size for the DMRL facility have been arrived at after carefully considering all the options available and keeping in view that the technology to be developed is meant for large scale commercial production of titanium sponge in the country. From the available literature it was seen that most of the commercial plants abroad were operating batch reactors with capacities ranging from 750-5000 kg. It was felt that a 2000 kg batch size will be an optimum choice for a 1000 T plant contemplated to meet the Indian demands. It was also felt that a prototype Kroll reactor of the same size should be tried out at the DMRL facility since it will be much simpler to set-up a larger plant subsequently by merely duplicating the design and specifications of the equipment selected and optimised at the DMRL facility.

Originally it was contemplated that DMRL will set up a demonstration facility which will be somewhat similar in scope to the NFC pilot-plant. However, considering that the Kerala Minerals & Metals Limited (KMML) were establishing a large scale facility for the production $TiCl_4$, it was decided that the DMRL facility should start from the chloride rather than from the mineral rutile.

The flow-sheet for DMRL process is shown in Fig. 3.

3.2 Chloride Purijcation

The pilot plant at NFC was equipped with batch distillation units for the purification of $TiCl_4$. While this approach had served the purpose of the NFC pilot plant, for large scale production it was essential to go-in for continuous purification. Keeping

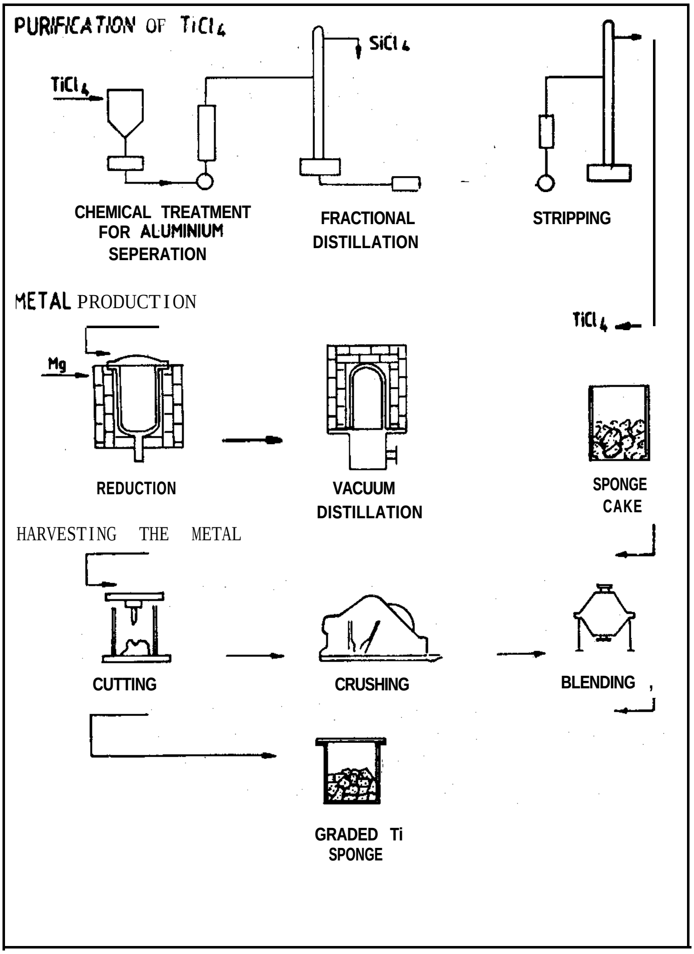

Figure 3. DMRL flow-sheet for large scale production of titanium sponge.

this requirement in view, a continuous chloride purification system has been designed for the DMRL facility. The raw chloride as received in steel drums is stored in large storage tanks of 25T capacity. With the help of specially designed pumps, the chloride from the 25T capacity tank is transferred to a treatment tank for the separation of aluminium chloride by controlled hydrolysis. The chloride is separated from the precipitated aluminium oxi-chloride using stainless steel filtration equipment and then stored in 10T capacity storage tanks. From this point onwards, the process has been designed for continuous operation. The chloride already separated from aluminium impurity is pre-heated to its boiling point and continuously fed to a packed bed distillation column fabricated from carbon steel for the separation of low boiling silicon tetrachloride. The $TiCl_4$ 'rich raffinate from the re-boiler is cooled and transferred to a surge tank from which it is again pumped through a heater to a stripper column fabricated entirely in AISI 304 type stainless steel. This column is

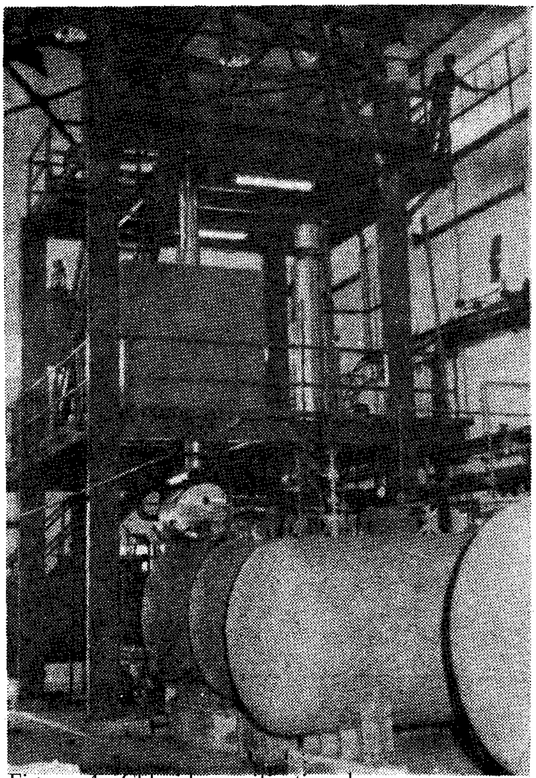

Figure 4. Chloride purification bay.

also of packed bed design. The product from the top of this column *is* pure $TiCl_4$ which after cooling is stored in 10T capacity stainless steel storage tanks. The entire process is designed for continuous production of pure chloride at the rate of 150 kg per hour, The equipment is well instrumented for measurement of temperatures, pressures, liquid levels, Row rates etc. Considering the hazardous nature of operations, pneumatic instruments with special materials of construction have been selected for trouble free performance. The process is also automated for maintaining a constant through-put through various items of equipment. The scheme has been designed for an input chloride of 99 8 per cent purity and an output chloride of 99.95 per cent purity as per details given in Table 3. An overall view of the chloride purification bay can be seen in Fig. 4.

3.3 *Kroll Reduction*

The pure chloride from the above storage tanks is pumped to the feed tank (Fig. 5) of the reduction reactor. From this tank the chloride is metered into the reduction retort and the instrumentation is designed to give continuous variation in the input in the range of O-300 kg per hour. This is an essential requirement for ensuring safe operation conditions in the reduction reactor.

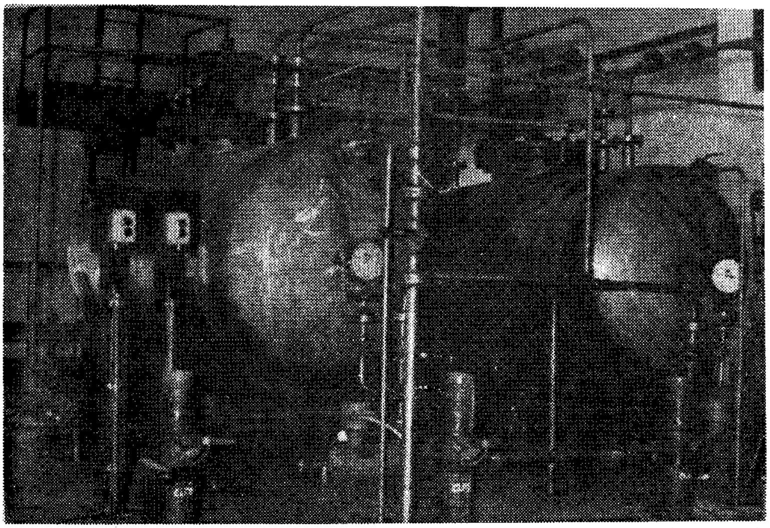

Figure 5. $TiCl_4$ feed tanks.

Table 3. Design basis for purification of titanium tetrachloride (Output rate : 150 kg/hr)

	Raw Chloride (%)	Pure Chloride (%)
$TiCl_4$	90.800 (min)	99.950 (min)
$SiCl_4$	0.050 (max)	0.003 (max)
$AlCl$	0.050 (max)	0.003 (max)
$VOCl_3$	0.005 (max)	0.003 (max)
Dissolved Gases and High Volatiles	0.020 (max)	0.003 (max)
Solids and Non-volatiles	0.080 (max)	0.003 (max)

The reduction equipment (Fig. 6) comprises a specially designed stainless steel retort and a crucible with a false bottom plate arrangement to serve as the reduction pot. For heating the retort a multi zone electric resistance furnace (Fig. 7) is used. For removal of the exothermic heat during reduction, the furnace is equipped with an air cooling system comprising a blower, a preheater and insulated duct work. For periodic tapping of molten magnesium chloride during reduction, a special tapping valve designed for high temperature service is fitted at the bottom of the retort.

Required quantity of pickled and dry magnesium is loaded into the retort and the same is evacuated with the help of an oil-sealed rotar ymechanical pump for complete

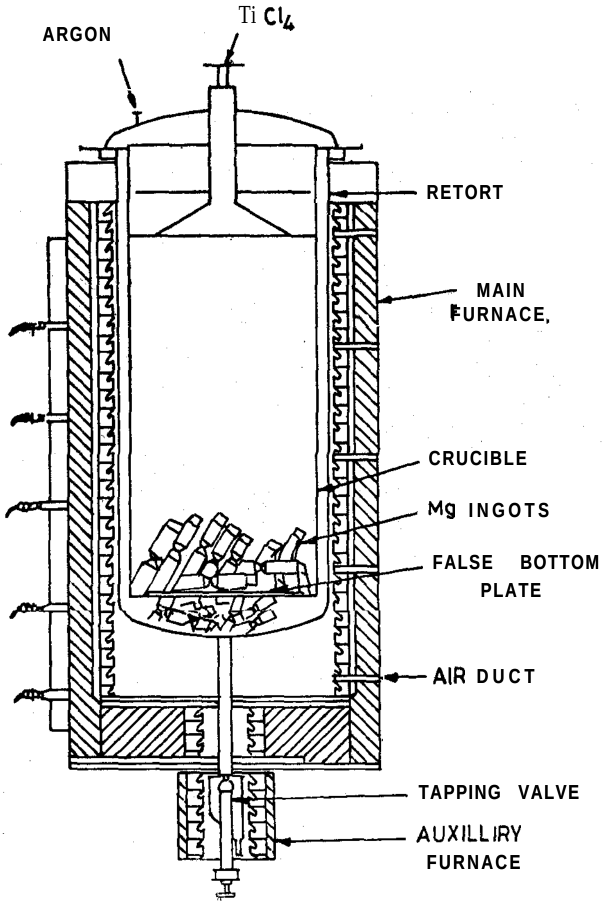

Figure 6. Reduction assembly.

elimination of air from the retort. The same is back filled with argon after ensuring leak tightness. After melting down the magnesium, liquid $TiCl_4$ is metered into the retort and the reduction is carried out in the temperature region of 800-875°C. Periodically the by-product $MgCl_2$ is tapped into specially designed moulds kept in a trolley. After solidification, this material *is* packed in standard 200 litre capacity air tight barrels. Nearly 8T of pure $TiCl_4$ is required per batch. The process is well instrumented for fully automatic and semi-automatic operation.

3.4 Vacuum Distillation

At the end of the reduction cycle, the reduction retort is lifted off the furnace and allowed to cool in a specially designed cooling bay (Fig. 8). For accelerating the cooling rate, water jets are provided. When the retort temperature reaches 70°C, the reduction pot is removed, thoroughly cleaned, weighed and loaded into the vacuum distillation unit (Fig. 9). The split type vacuum distillation retort is fabricated from

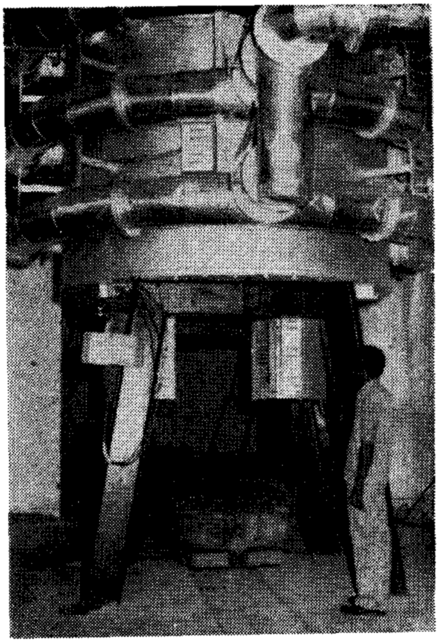

Figure 7. Reduction furnace.

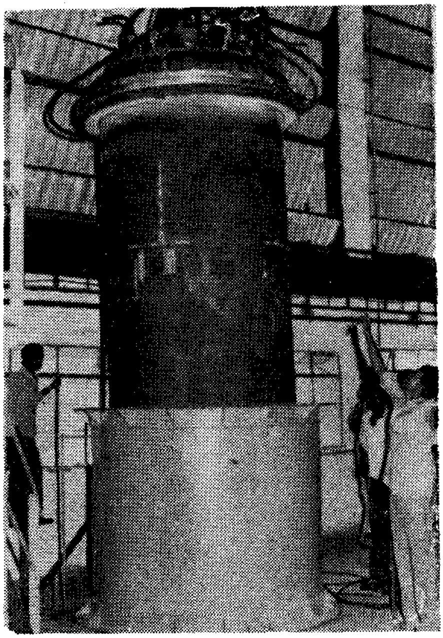

Figure 8. Reduction retort in cooling station.

heat resistant stainless steel and the top section of the retort is heated by a bell type vacuum furnace (Fig. 10). The retort is evacuated to a pressure of about 10^{-3} mm *Hg* with the help of a specially selected high vacuum pumping system. The furnace side is also evacuated by a separate mechanical pump for ensuring a long operating life for the retort at the operating temperature and vacuum by maintaining the differential pressure across the retort wall in the region of only 10 to 20 mm *Hg* absolute. After initial evacuation at room temperature and leak testing, the top section of the retort housing the reduction crucible is heated to a temperature of 950-1000°C for separation of residual magnesium chloride and excess magnesium from the sponge. At the end of the cycle, the furnace is switched off, cooled to 600°C and lifted off the retort after back-filling the retort with argon and the furnace with air. For accelerating the cooling rate, the retort is then sprayed with cooling water. When the crucible temperature is in the region of 50°C, the same is discharged from the retort and transferred to the sponge handling section.

3.5 Sponge Handling

The sponge cake (Fig. 11) is carefully extracted from the crucible and cut to lumps of 200 mm size in a 200 T hydraulic press. At this stage any discoloured material is discarded after visual inspection so that the product quality is ensured, The large lumps of sponge are then crushed to finished size of 12 mm to + 2 mm in a series of two jaw

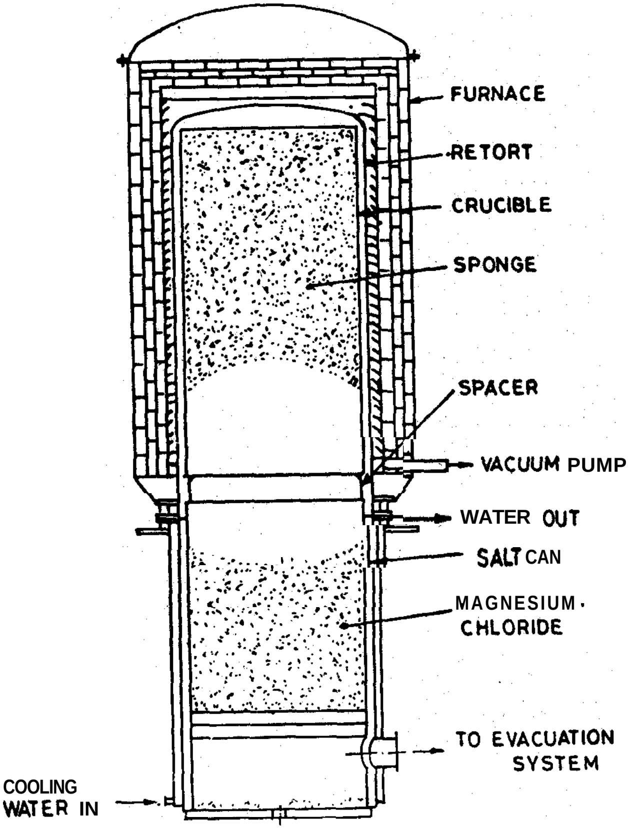

Figure 9. Vacuum distillation assembly.

crushers coupled with vibrating screens (Fig. 12). The finished product (Fig. 13) after analysis is blended to desired specifications in a double cone blender and packed in steel drums of 200 kg capacity under a protective cover of argon.

3.6 Engineering Consultancy

Considering the tight time schedule envisaged for this project, M/s. Engineers India Limited (EIL) were appointed as consultants to assist DMRL mainly in (i) civil and structural works; (ii) internal and external power distribution system; (iii) utilities such as process water, cooling water, compressed air etc. The assistance of ETL was also sought in regard to mechanical design of reduction and vacuum distillation retorts/ assemblies as well as process design of the continuous purification system described above.

3.7 Production Trials

Trial operations on production of the metal in 1500 to 2000 kg batches are in progress using pure **degassed/distilled** $TiCl_4$ and pickled magnesium. Results obtained so far are

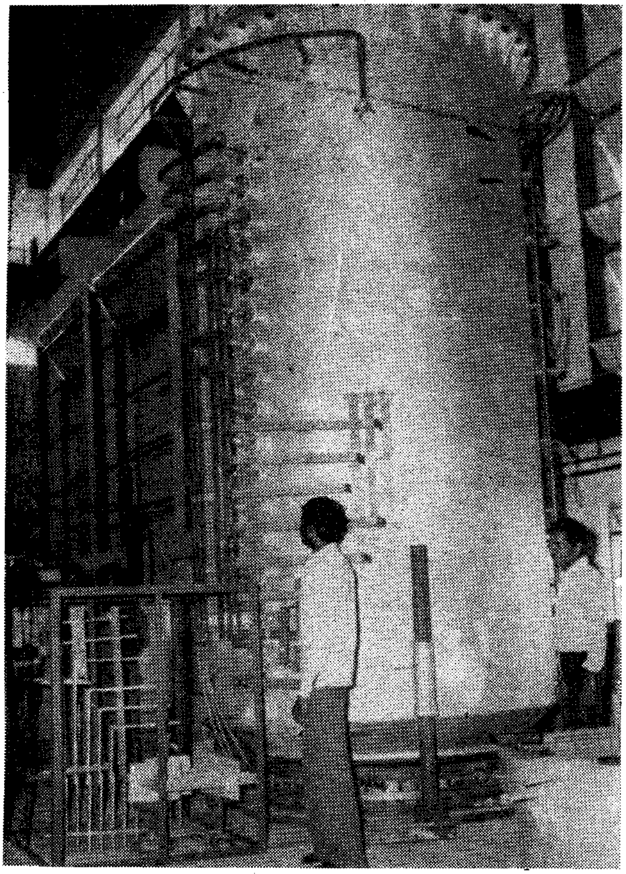

Figure 10. Vacuum distillation furnace.

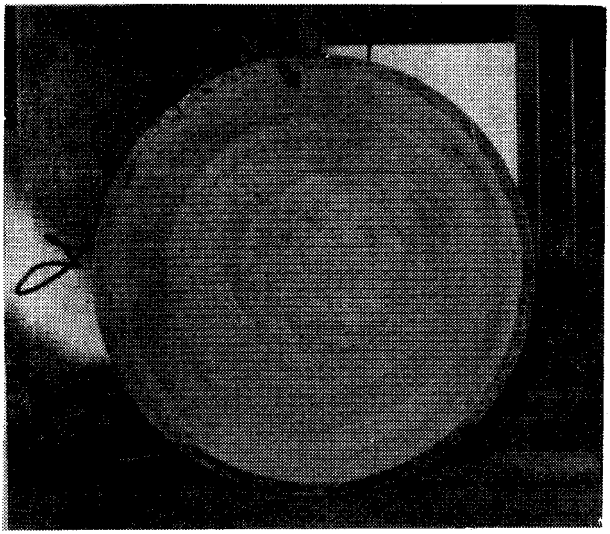

Figure 11. Titanium sponge cake in crucible.

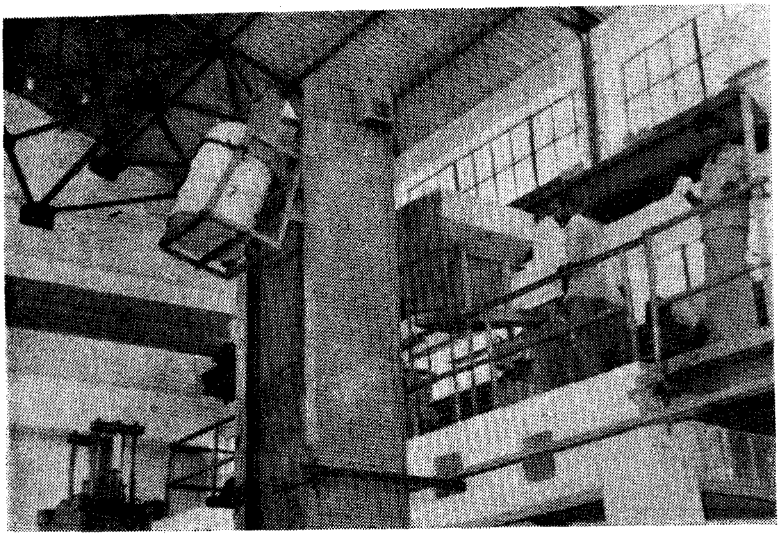

Figure 12. Sponge crushing.

Figure 13. Crushed titanium sponge.

encouraging in respect of sponge quality. Table 4 compares the ASTM specification for titanium sponge with the values obtained from one of the batches recently produced in the DMRL facility. Plans are afoot to study alternative materials of construction for the crucible/retort and to streamline the production operations. Attempts are also being made to incorporate a computer based data acquisition-cum-control system for various operations.

4. Conclusions

The development of technology for the production of *Ti* sponge in the country has been continuing for more than three decades. With the commissioning and successful

Table 4. Quality of titanium sponge produced at DMRL facility.

Impurity **(max)**	ASTM grade MD 120	DMRL sponge
	(Values in parts per million)	
Nitrogen	0.015	0.002
Carbon	0.020	0.018
Magnesium	0.0’0	0.030
Chlorine	0.120	0.011
Iron	0.120	0.008
Silicon	0.040	0.010
Hydrogen	0.010	0.003
Oxygen	0.100	0.060
BHN (hardness)	120	**90/95**

operation of the demonstration plant at DMRL, the technology for large scale production of titanium is placed on a firm footing. The day is not too far when commercial operations will commence and place India in the world map of titanium-not only to cater to the indigenous needs, but also for exports to earn valuable foreign exchange.

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